

**Water Resources Research Center
Annual Technical Report
FY 2012**

Introduction

Since its founding, the University of Arizona's Water Resources Research Center (WRRC) has become a hub for water resources research and information transfer in Arizona. Its mission is to promote understanding of critical state and regional water management and policy issues through research, community outreach and public education. A Research and Extension unit of the College of Agriculture and Life Sciences, the WRRC is the designated state water resources research institute established under the 1964 Federal Water Resources Research Act. As such, the WRRC administers research grant programs, conducts water management and policy research, and runs a strong information transfer program that includes publications, presentations, conferences and other public events. In addition to its activities pursuant to the WRRRA, the WRRC carries out research on water-related topics of policy interest to the State and beyond. The WRRC accomplishes its mission through multiple collaborations and cooperative arrangements. It is the home of the Water Sustainability Program, one of three programs making up the Water, Environmental and Energy Solutions (WEES) program, funded from the UA's Technology and Research Initiative Fund (TRIF). The WRRC is also the home for Arizona Project WET (Water Educations for Teachers); initiated at the WRRC in 1991, APW is Arizona's premier water education program. As a Research and Extension unit, the WRRC maintains a mutually beneficial relationship with the Cooperative Extension system.

Research Program Introduction

The University of Arizona's WRRC provides support in the form of research grants for investigators at all three state universities in Arizona, through the WRRRA, Section 104(b) research grant program. Each year, the WRRC typically funds three or four small projects to examine water issues of statewide importance. A wide range of projects have been funded over the years. In the last few years, projects have emphasized improvements in water supply reliability and quality, and explored new ideas to address water problems or expand understanding of water and water-related phenomena. In the project year, proposals were encouraged that addressed the research recommendations of the Arizona Governor's Blue Ribbon Panel on Water Sustainability. These recommendations focused attention on contaminants of emerging concern.

During the project year (March 2012 through February 2013) the WRRC funded three projects proposed by University of Arizona investigators. One project examined the attenuation of engineered nanoparticles in treated wastewater as a result of soil aquifer treatment. A second project investigated the effect of solids retention time in the wastewater treatment process on antibiotic resistance. The third project focused attention on suspended solids and sediments downstream of wastewater treatment plant discharges. Researchers evaluated the endocrine disruption activity and cytotoxicity in solid phase samples.

The WRRC also administers any WRRRA National Competitive Grant (104(g)) awarded to researchers in Arizona. In 2010, Ty Ferre, UA Department of Hydrology and Water Resource, was awarded a three-year grant for the project "Improving Hydrologic Investigations through Multi-Model Analysis and Discriminatory Data Collection."

A cooperative agreement with the U.S. Geological Survey supported continuing progress on The U.S.-Mexico Transboundary Aquifer Assessment Program, which built on binational discussions to develop parallel reports to the U.S. Congress on activities to date in each of the two priority aquifers.

Cooperative Agreement No. 08HQAG0058 Transboundary Aquifer Assessment Program

Basic Information

Title:	Cooperative Agreement No. 08HQAG0058 Transboundary Aquifer Assessment Program
Project Number:	2008AZ366S
Start Date:	3/17/2008
End Date:	3/16/2013
Funding Source:	Supplemental
Congressional District:	AZ-7
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Management and Planning, None
Descriptors:	
Principal Investigators:	Sharon Megdal, Christopher A Scott

Publications

1. Megdal, Sharon B. 2007. "Front-Row View of Federal Water Lawmaking Shows Process Works – U.S. Mexico Transboundary Aquifer Assessment Act Pondered, Passed and Signed," Arizona Water Resource, January-February 2007.
2. Megdal, Sharon B. 2008. "Front-Row View of Federal Water Lawmaking Shows Process Works – U.S. Mexico Transboundary Aquifer Assessment Act Pondered, Passed and Signed" (updated/revised version of 2007 column), in Norman, Laura M., Hirsch, Derrick D., and Ward, A. Wesley, eds., 2008, Proceedings of a USGS Workshop on facing tomorrow's challenges along the U.S.-Mexico border; monitoring, modeling, and forecasting change within the Arizona-Sonora transboundary watersheds: U.S Geological Survey Circular 1322, <http://pubs.usgs.gov/circ/1322/>.
3. Scott, Christopher A., et al. 2009. "Assessment of United States – Mexico Transboundary Aquifers Facing Climate Change and Growth in Urban Water Demand" Climate Change (in press)
4. Megdal, Sharon B., 2007. "Front-Row View of Federal Water Lawmaking Shows Process Works – U.S. Mexico Transboundary Aquifer Assessment Act Pondered, Passed and Signed," Arizona Water Resource, January-February 2007.
5. Megdal, Sharon B., 2008. "Front-Row View of Federal Water Lawmaking Shows Process Works – U.S. Mexico Transboundary Aquifer Assessment Act Pondered, Passed and Signed" (updated/revised version of 2007 column), in Norman, Laura M., Hirsch, Derrick D., and Ward, A. Wesley, eds., 2008, Proceedings of a USGS Workshop on Facing Tomorrow's Challenges Along the U.S.-Mexico Border; monitoring, modeling, and forecasting change within the Arizona-Sonora transboundary watersheds, U.S Geological Survey Circular 1322, <http://pubs.usgs.gov/circ/1322/>.
6. Scott, Christopher A., Sharon Megdal, Lucas Antonio Oroz, James Callegary, Prescott Vandervoet 2009. "Assessment of United States – Mexico Transboundary Aquifers Facing Climate Change and Growth in Urban Water Demand" Climate Change (in review).
7. Scott, Christopher A., Sharon Megdal, Lucas Antonio Oroz, Martin Mexía, Hildebrando Ramos, 2008. "Building Shared Vision: assessment of transboundary aquifers along the United States – Mexico border." In Proceedings of International Conference on Water Scarcity, Global Changes, and Groundwater Management Responses, University of California – Irvine, UNESCO, USGS, Irvine, CA, December 1st to 5th, 2008.

Cooperative Agreement No. 08HQAG0058 Transboundary Aquifer Assessment Program

8. Vandervoet, Prescott L., 2009. "Transboundary Aquifer Assessment Program Arizona," Annual Meeting for the Association for Borderlands Studies. Albuquerque, New Mexico, April 16, 2009.
9. Milman, Anita, Christopher A. Scott, 2010. "Beneath the Surface: Intra-National Institutions and Management of the United States – Mexico Transboundary Santa Cruz Aquifer," *Environment and Planning C: Government and Policy*. In press.
10. Megdal, Sharon B., 2007, "Front-Row View of Federal Water Lawmaking Shows Process Works – U.S. Mexico Transboundary Aquifer Assessment Act Pondered, Passed and Signed," *Arizona Water Resource*, January-February 2007.
11. Megdal, Sharon B., 2008, "Front-Row View of Federal Water Lawmaking Shows Process Works – U.S. Mexico Transboundary Aquifer Assessment Act Pondered, Passed and Signed" (updated/revised version of 2007 column), in Norman, Laura M., Hirsch, Derrick D., and Ward, A. Wesley, eds., 2008, *Proceedings of a USGS Workshop on Facing Tomorrow's Challenges Along the U.S.-Mexico Border: monitoring, modeling, and forecasting change within the Arizona-Sonora transboundary watersheds*, U.S Geological Survey Circular 1322, <http://pubs.usgs.gov/circ/1322/>.
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19. Milman, A., C.A. Scott, 2010., *Beneath the surface: intranational institutions and management of the United States – Mexico transboundary Santa Cruz aquifer*. *Environment and Planning C: Government and Policy* 28: 528-551.
20. Norman, Laura M., Lainie Levick, Phillip D. Guertin, James Callegary, Jesus Quintanar Guardarrama, Claudia Zulema Gil Anaya, Andrea Prichard, Floyd Gray, Edgar Castellanos, Edgar Tepezano, Hans Huth, Prescott Vandervoet, Saul Rodriguez, Jose Nunez, Donald Atwood, Gilberto Patricio Olivero Granillo, Francisco Octavio Gastelum Ceballos, 2010, "Nogales Flood Detention Study" U.S. Geological Survey Open File Report 2010-1261.
21. Vandervoet, P.L., S.B. Megdal, C.A. Scott, 2011, *Los acuíferos transfronterizos Santa Cruz y San Pedro de Arizona y Sonora: Estado actual y creación de bases de datos (The Santa Cruz and San Pedro transboundary aquifers of Arizona and Sonora: Current status and database creation)* In G. Cordova, J. Dutram, B. Lara, and J. Rodriguez (Eds.) *Fortaleciendo el diálogo social: El desarrollo humano transfronterizo en la región Sonora-Arizona (Strengthening social dialogue: Transboundary human development in the Sonora-Arizona region)* Universidad de Sonora. Hermosillo, Sonora, Revise and resubmit in process.
22. Alley, W.M., ed., 2013, *Five-year interim report of the United States – Mexico Transboundary Aquifer Assessment Program: 2007 – 2012: U.S. Geological Survey Open-File Report 2013-1059*, 31

Cooperative Agreement No. 08HQAG0058 Transboundary Aquifer Assessment Program

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23. Callegary, J., Megdal, S.B., Scott, C.A., Vandervoet, P.L., 2013, Arizona/Sonora Section of the Transboundary Aquifer Assessment Program, in USGS Open File Report 2013-1059, 14 p.
 24. dos Santos, Plácido, 2012, The Transboundary Aquifer Assessment Program (TAAP) in Arizona-Sonora / Programa para la Evaluación de Acuíferos Transfronterizos en Sonora-Arizona. Water Resources Research Center, 4p. Available at <http://wrrc.arizona.edu/sites/wrrc.arizona.edu/files/pdfs/TAAP%20Brochure%20Final%2023April2013.pdf>

Summary

The Transboundary Aquifer Assessment Program (TAAP) originates from U.S. Public Law 109-448, signed into law by the President of the United States on December 22, 2006 as the U.S.-Mexico Transboundary Aquifer Assessment Act. The Act applies to the states of Texas, New Mexico, and Arizona where four transboundary aquifers have been designated for priority assessment. These aquifers include the Hueco Bolson and Mesilla Basin aquifers in the greater El Paso / Ciudad Juárez region and the Santa Cruz and San Pedro aquifers across the Arizona – Sonora border (see map). TAAP is designated to operate for 10 years, with \$50 million authorized for appropriation over that time period. Appropriations to date include \$500,000 each for fiscal years 2008 and 2009 and \$1 million for 2010. By 2012 a total of only \$2 million had been appropriated for all four of the priority aquifers designated in the federal legislation. With no appropriations for 2013 or later, the program's remaining funding expired on March 15, 2013. Unless additional funds materialize for continuation of the program, this will be the final report provided by the University of Arizona (UA) Water Resources Research Center (WRRC.)



TAAP-A/S (Arizona/Sonora) conducts assessments of aquifers shared by Arizona and Sonora as a collaborative effort between the United States Geological Survey (USGS) and the University of Arizona, by way of the WRRC and the Udall Center for studies in Public Policy. A variety of other U.S. and Mexican stakeholders participate in the priority- setting for the assessment process. TAAP-A/S (which studies the transboundary Santa Cruz and San Pedro aquifers) has participated in the UNESCO Internationally Shared Aquifer Resource Management (ISARM) Programme, which has led to TAAP participation in international conferences and a wider range of scientific resources.

During the November 2009 international TAAP workshop, the Transboundary Aquifer Assessment Program- Arizona and Sonora component developed a work plan for activities to be carried out during the 2010-11 program year. These activities were divided between responsibilities falling under the supervision of the Arizona Water Science Center of the USGS and those by the Water Resources Research Center (WRRC) and Udall Center for Studies in Public Policy (Udall), both at the University of Arizona. Activities carried out by the WRRC and Udall are classified under the heading of “vulnerability assessment” as they are focus on issues more closely related to groundwater use by and related to human populations. Activities supervised by the USGS come under the heading of “hydrological modeling framework”, as the work tends to focus on the purely hydrological and geological aspects of aquifers in question. The vulnerability assessment items (listed below in bold) aim to involve a varied socio-economic set of stakeholders that affect and depend upon groundwater resources located within the bi-national upper Santa Cruz and San Pedro river basins.

The evolving vulnerability related to groundwater use by urban centers such as Cananea, Sierra Vista, and Ambos Nogales, as well as surrounding rural communities and a proposed mine in the Mexican portion of the Santa Cruz Aquifer, is a significant issue for transboundary aquifers, given the proximity of aforementioned cities to the international boundary as well as their near total dependence on groundwater. Some of the issues particular to these areas include groundwater recharge deficit in the

Sierra Vista subwatershed, over-allotment of groundwater rights in the Mexican section of the San Pedro, storm runoff and wastewater (conveyance and treatment) infrastructure in Nogales, Sonora, and uncertainty regarding groundwater bearing and defining geological units around Nogales, Arizona well fields. Given these, as well as other unique regional issues, the vulnerability assessment for the TAAP-A/S work plan for project year 2012-13 focused on the following activities:

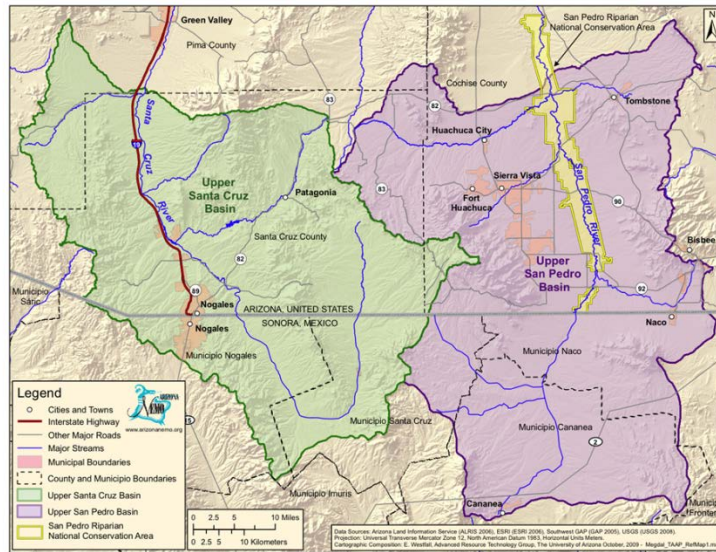
- A. Engagement with Mexican Project Partners
- B. Development of Binational GIS Products
- D. Development of Draft Reports for the San Pedro and Santa Cruz Aquifers
- C. Improved linkages with international best practices (via ISARM)

A. Engagement with Mexican Project Partners.

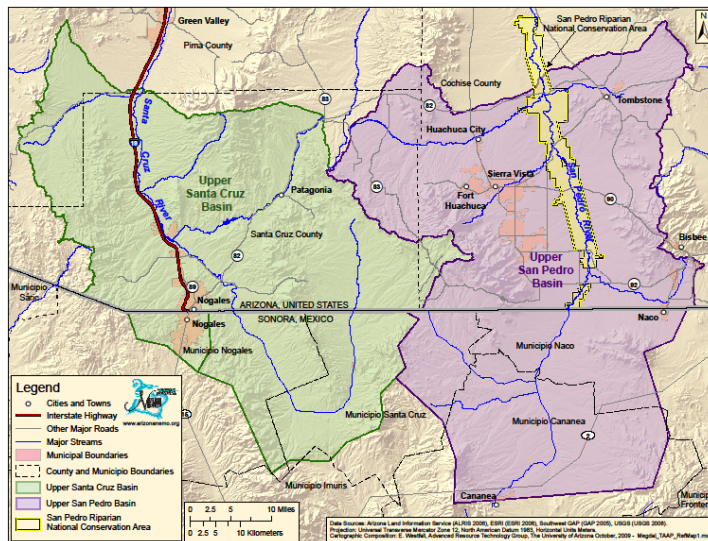
Activity description (2012-13 work plan): After a hiatus of Arizona-Mexico engagement on the TAAP's technical matters, the U.S. project partners reinvigorated bilateral discussions regarding the program to focus efforts on production of binational reports for the San Pedro and Santa Cruz Basins. Close binational coordination was needed among the USGS, University of Arizona, the University of Sonora, Mexico's National Water Commission and the International Boundary and Water Commission.

Summary of Activities Completed:

- The UA WRRC developed a new bilingual brochure describing the TAAP for use in Mexico and the U.S. The brochure is available at the UA WRRC's website:
<http://wrrc.arizona.edu/sites/wrrc.arizona.edu/files/pdfs/TAAP%20Brochure%20Final%2023April2013.pdf>
- The UA's TAAP representatives participated in the International Boundary and Water Commission's 2012 Binational Border Water Resources Summit in September 2012. The Summit's Recommendations and Conclusions cited a need to continue funding for *"the critical Transboundary Aquifer Assessment Program (TAAP), a cooperative Mexican-U.S. research project."*
- The renewed binational engagement that occurred during 2012 brought to light some significant differences regarding the project boundaries. As a result of this bilateral re-examination of the project boundaries, Mexican partners revised the project boundaries in both the San Pedro and Santa Cruz study areas to reflect the regulatory "aquifer" boundaries defined by CONAGUA for administrative purposes. The original project boundaries and the final project boundaries, which were adopted during 2012, are reflected on the Arizona-Sonora TAAP study area maps below.



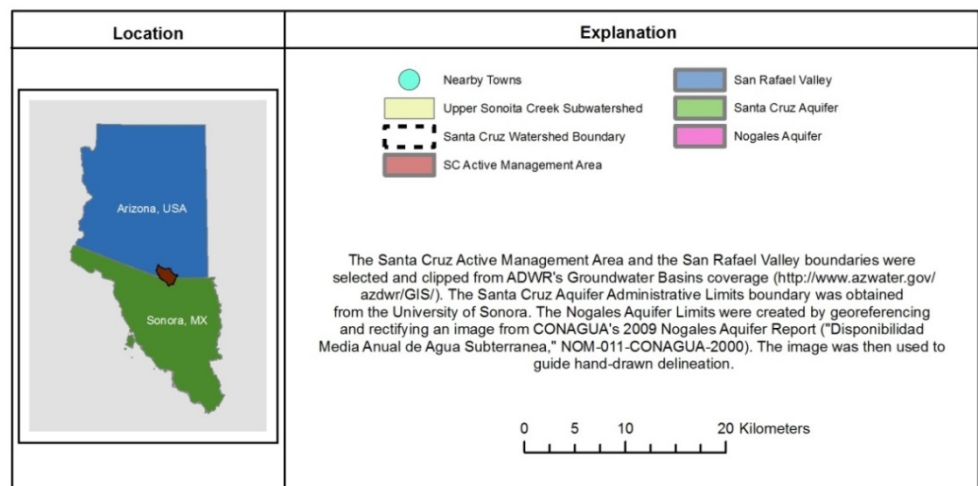
Map above depicts the project boundaries prior to 2012 bilateral engagement.



This map depicts the final project boundaries after 2012 bilateral engagement.

- In the re-examination of the technical scope of the binational assessments in the Arizona-Sonora region, another notable difference of interpretation came to light that required several months for resolution. At issue was the proposed exclusion of the Mexican portion of the Nogales Wash watershed. For regulatory purposes Mexican authorities define the Santa Cruz Aquifer as an administrative region which does not include the Nogales watershed. Consequently, the University of Sonora was contracted by the Mexican Section of the IBWC to perform a TAAP study of the Santa Cruz Aquifer, not including the Nogales Aquifer region. Although not considered to be a part of the Santa Cruz Aquifer, the involved parties recognized the hydrogeological connectivity of these two areas and concluded that both would be part of the Santa Cruz Aquifer TAAP study. The following map depicts the five regulatory subsets that were included in the Santa Cruz Aquifer TAAP study.

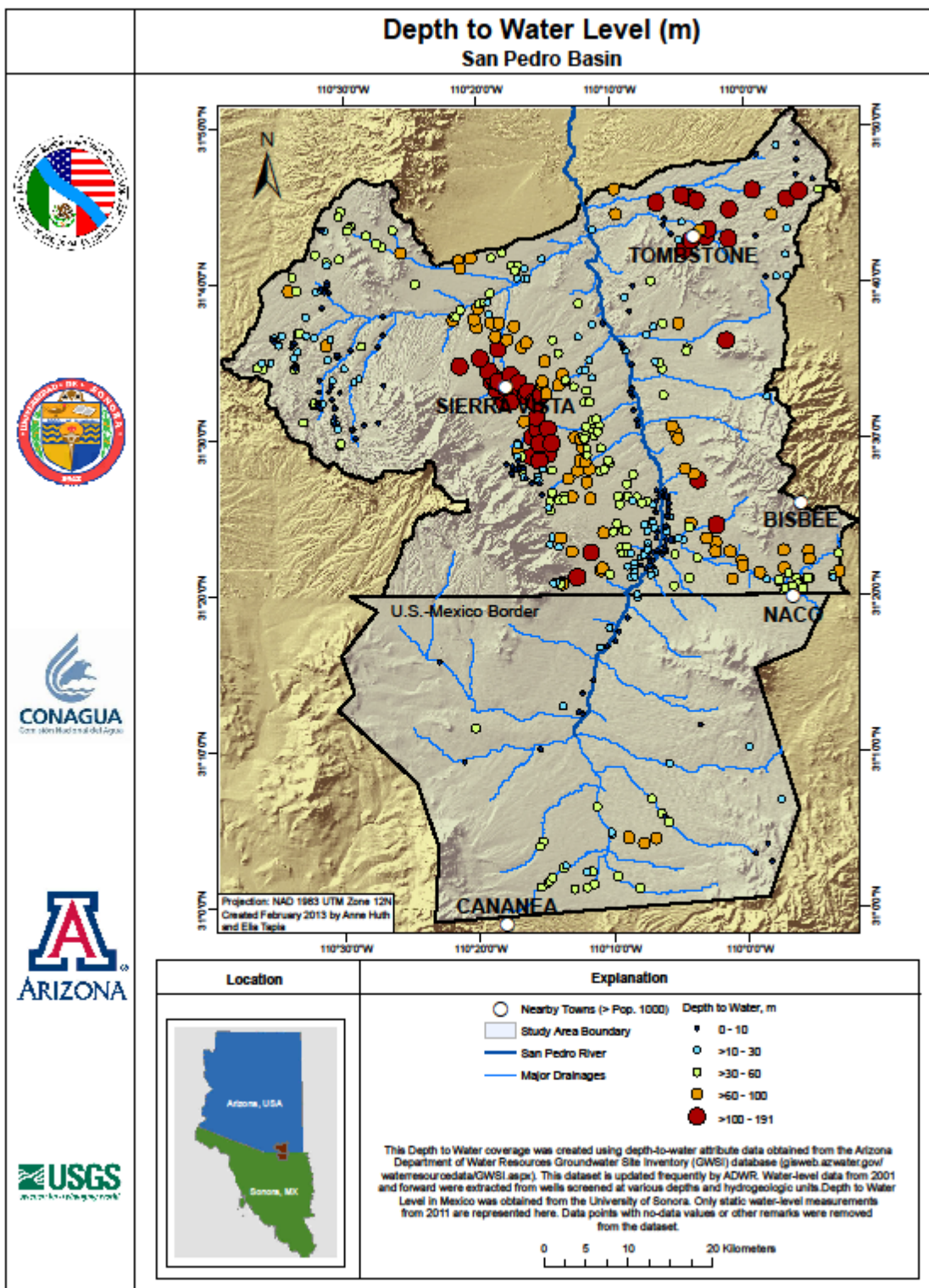
Regulatory Subsets of Study Area Santa Cruz Basin

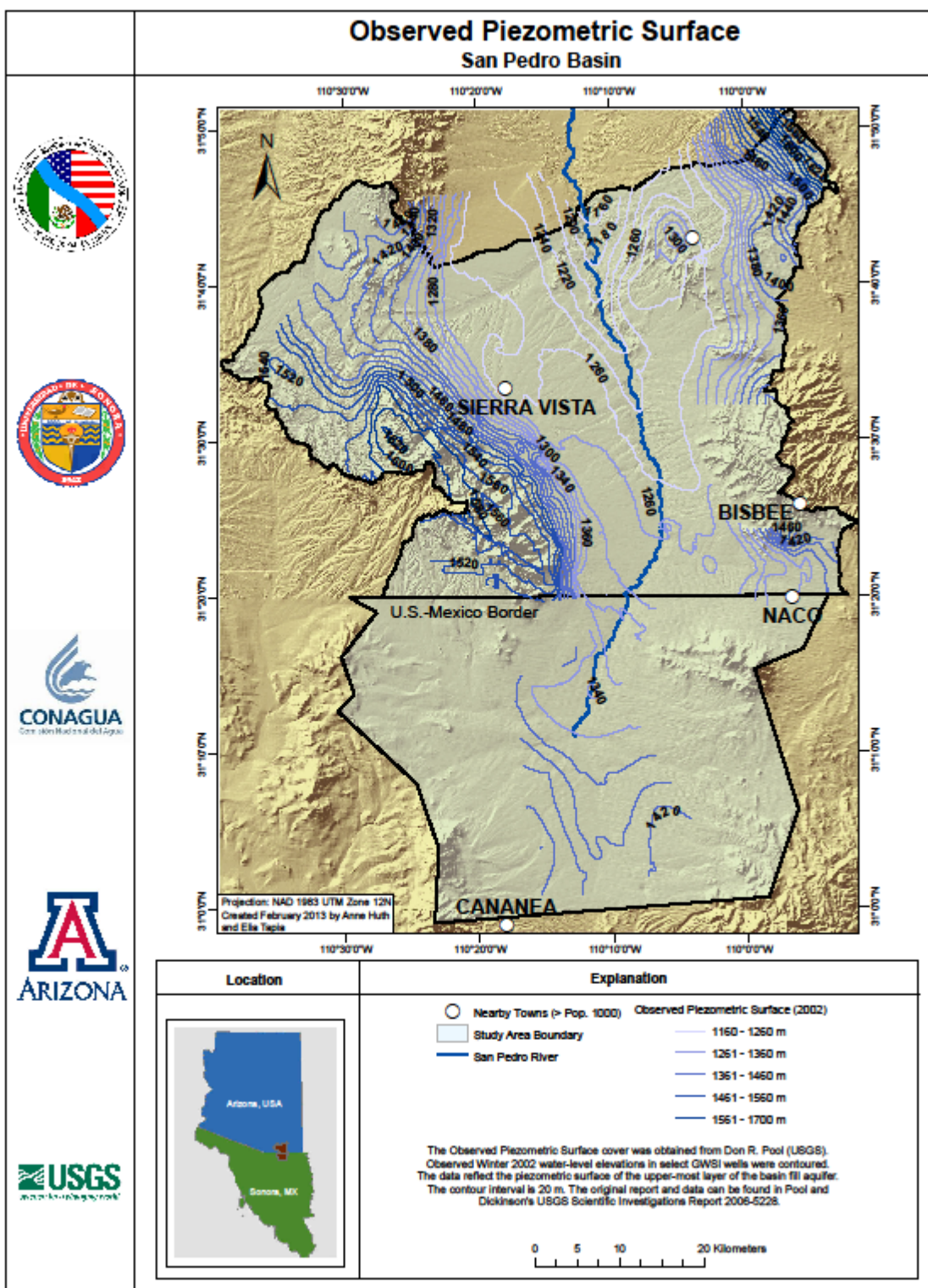


B. Development of Binational GIS Products

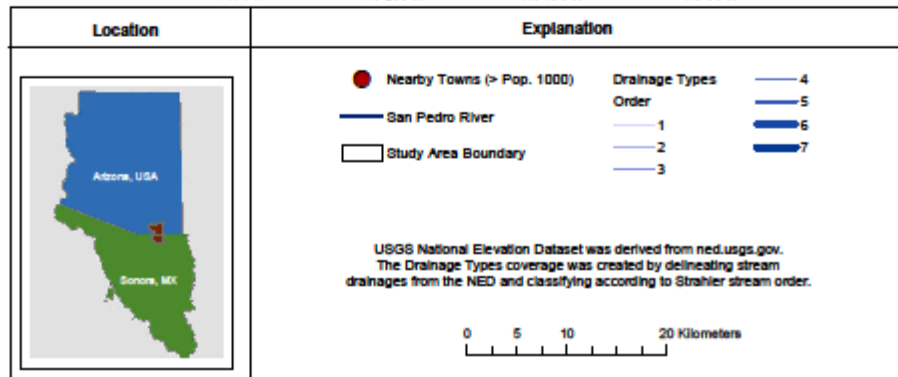
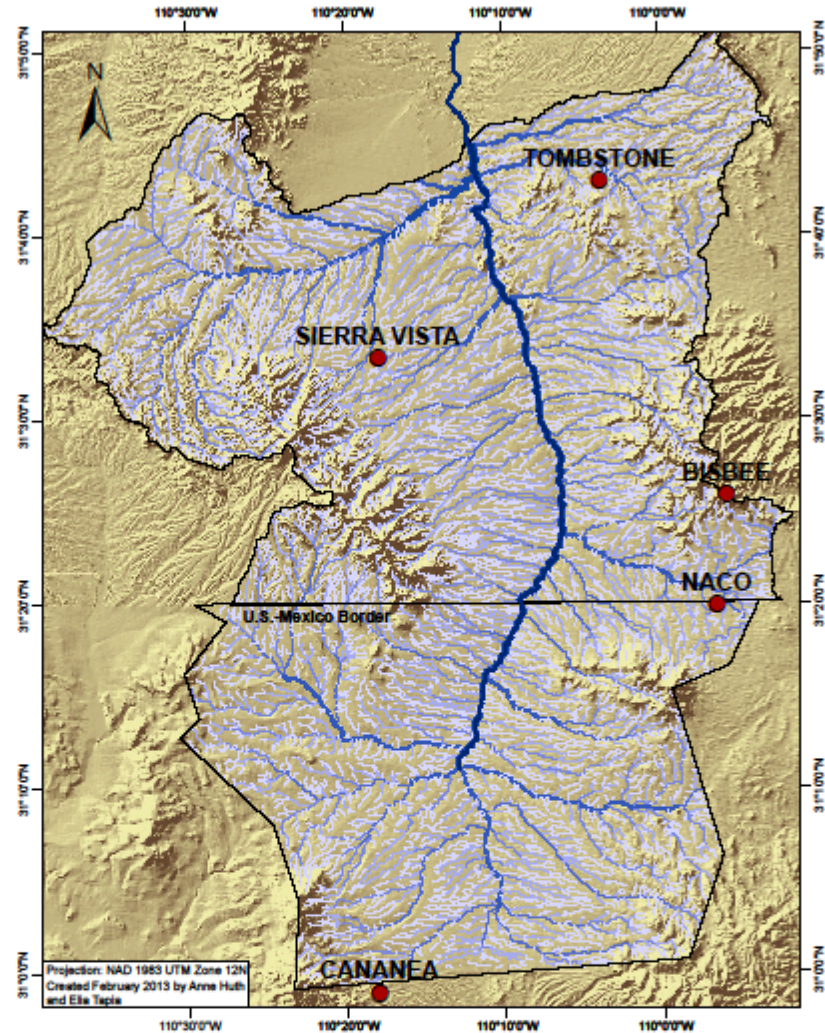
Activity description (2012-13 work plan): The UA WRRC awarded a contract for professional services to generate a series of binational GIS products for the TAAP effort in the Arizona-Sonora region. The contractor accessed GIS data layers archived with the USGS Water Science Center in Tucson as well as host of other data sets from locations such as the Arizona Department of Water Resources, the University of Sonora and other organizations as needed. The general categories of data handled by the contractor included geology, geophysics, land use, land cover, hydrology, hydrogeochemistry and climatic information. A total of over 60 GIS maps were generated, each map was accompanied by documented metadata and a database of all data sources used in the production of the maps. When finalized binationally for inclusion in the TAAP reports for the San Pedro and Santa Cruz aquifers, the maps, databases and metadata will all be posted at the IBWC's website since the reports will be binationally approved.

The binational maps that have been produced have never been attempted before and represent a level of bilateral data-sharing and collaboration that is precedent-setting along the U.S.-Mexico border. Several examples of the maps are included below. The complete data sets are archived as working files in the USGS, University of Sonora and the UA WRRC.

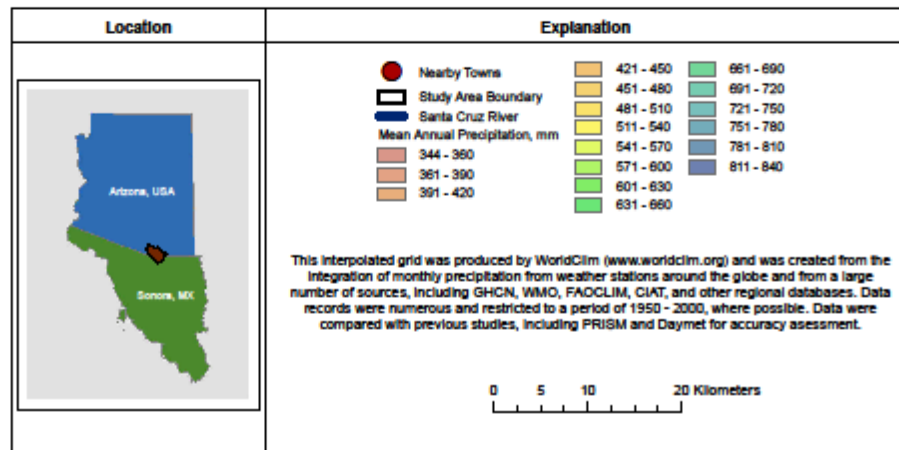
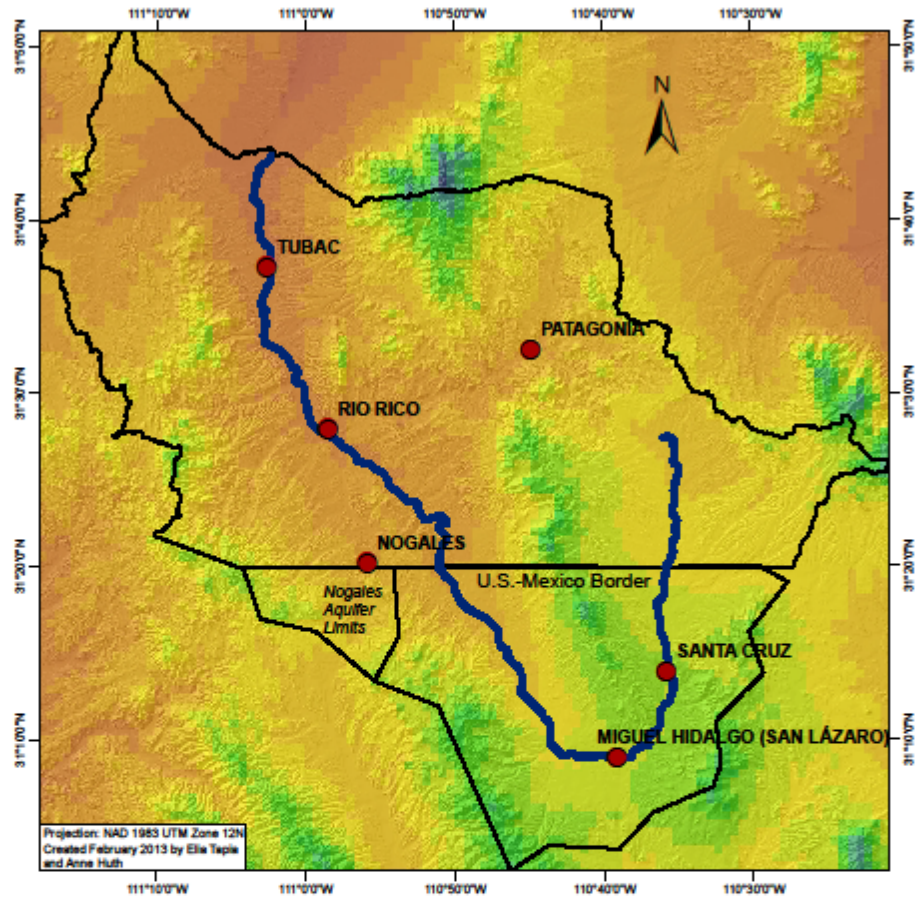




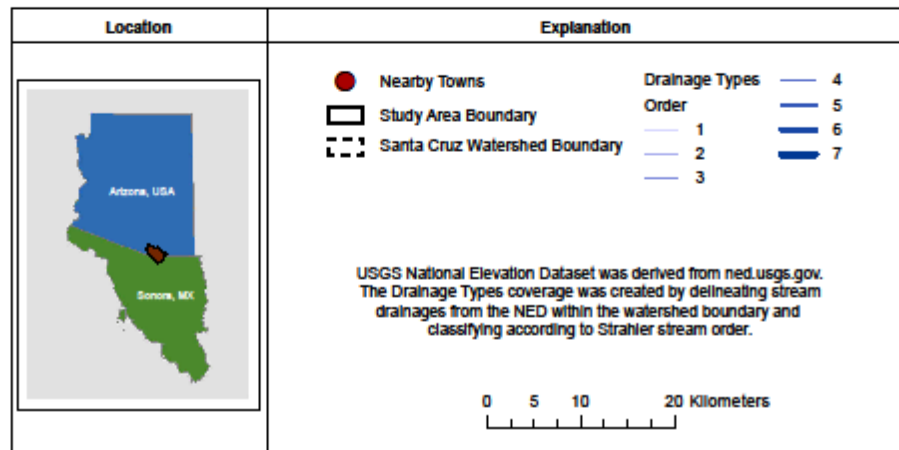
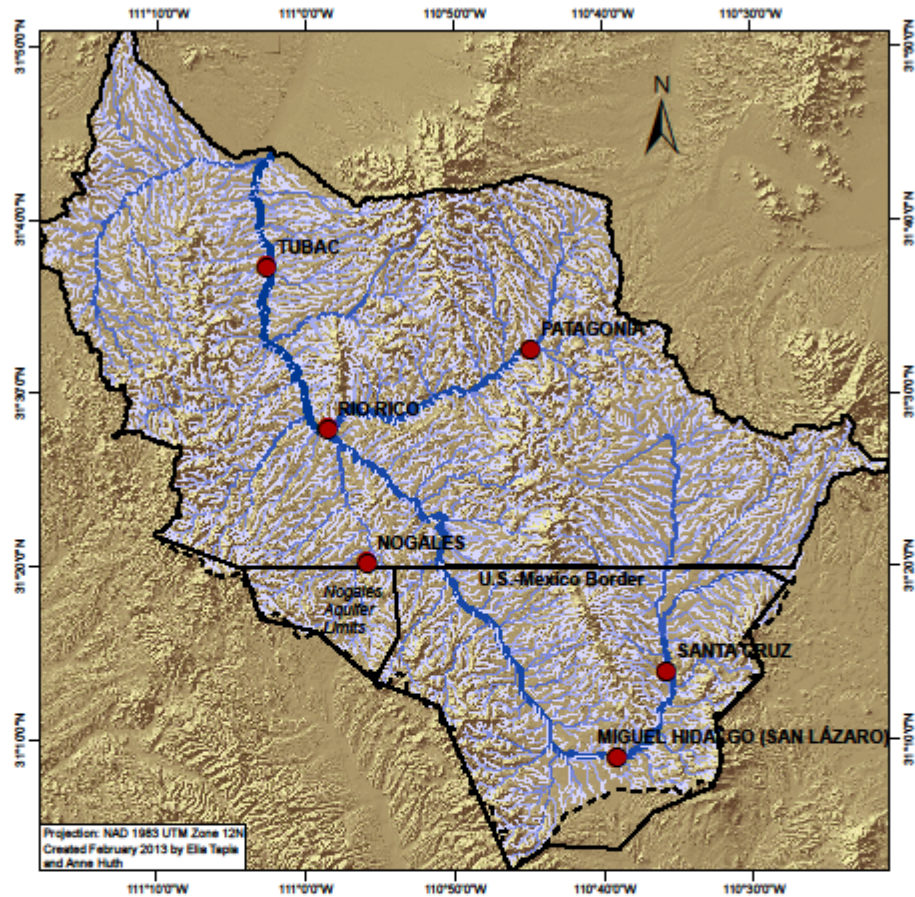
Drainage Types San Pedro Basin



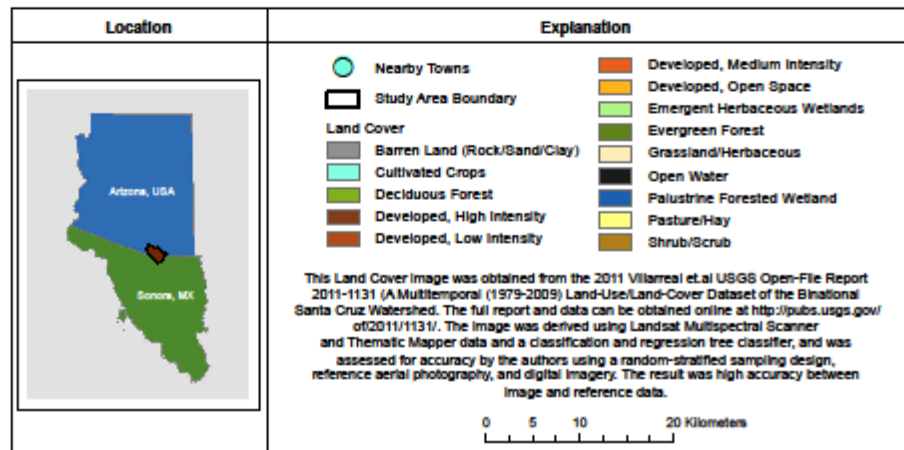
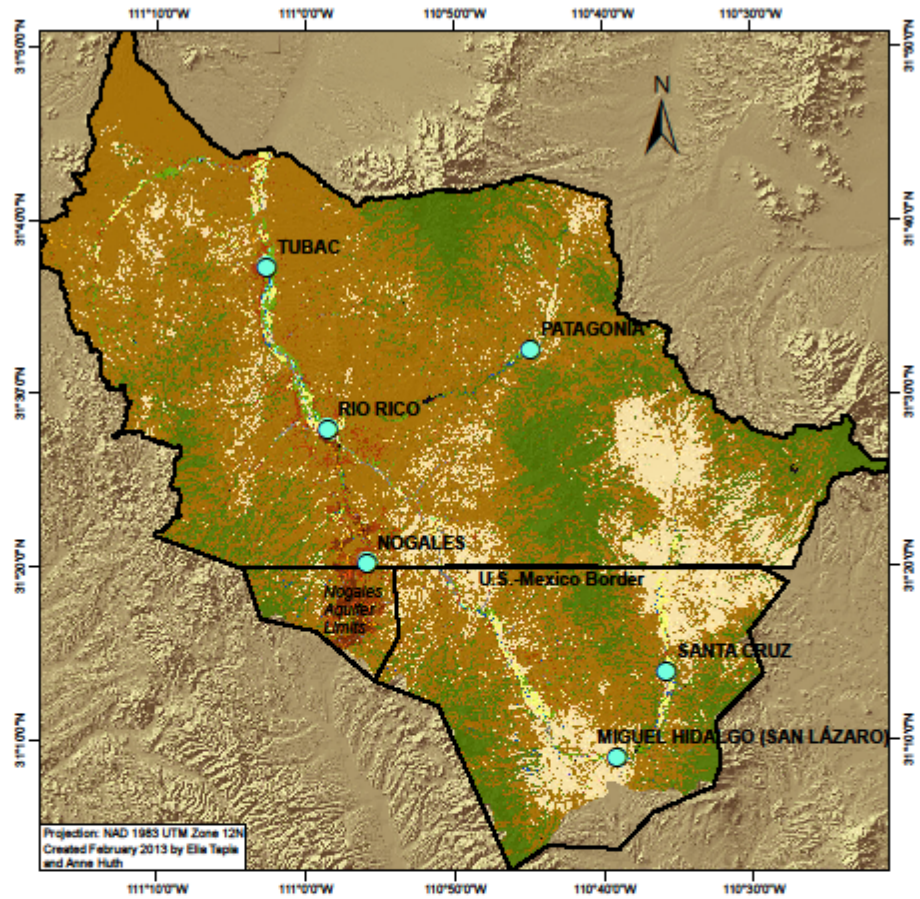
Mean Annual Precipitation (mm) Santa Cruz Basin



Drainage Types Santa Cruz Basin



Land Cover Santa Cruz Basin



C. Development of Draft Reports for the San Pedro and Santa Cruz Aquifers

Activity description (2012-13 work plan): The U.S. and Mexico participants in the Arizona-Sonora TAAP program, met during early 2012 and reached agreement on details regarding two reports that would be developed during the period 2012-2013. The parties were the USGS, Mexico's National Water Commission (CONAGUA), the University of Sonora's Department of Geology (UNISON), the University of Arizona Water Resources Research Center (UA WRRC) and the university's Udall Center for Public Policy, and the International Boundary and Water Commission's U.S. and Mexico Sections. The USGS, UNISON and UA WRRC agreed to write separate draft reports of the San Pedro and Santa Cruz aquifers during this year-long planning period. The authors would write in a single language, Spanish, in order to minimize translation needs and to facilitate the exchange of interim draft products. The parties also reached consensus on the outline that would be used for both reports. The English translation of the binationally adopted outline is presented below:

Prologue

Executive Summary

1. Introduction
 - i. Background
 - ii. Objectives
 - iii. Prior Studies
 - iv. Geographical Setting
 - v. Binational Socioeconomic Context
 - vi. Water Use
 - vii. Development Activities
 - viii. Methodologies and Techniques Used
2. Physiography, Climate
 - i. Physiographic Province
 - ii. Hydrography
 - iii. Hypsometry
 - iv. Terrain Slopes
 - v. Regional Climatic System
 - vi. Soils
 - vii. Vegetation
3. Hydrology, Hydrometeorology and Hydrogeomorphology
 - i. Climatological Analysis
 - ii. Precipitation and Evapotranspiration
 - iii. Surface Water Hydrology
 - iv. Drainage Types and Maximum Stream Order
 - v. Land Use and Other Land Cover Types
 - vi. Hydrogeomorphic Units
4. Conceptual Geologic Model
 - i. Regional Geologic Context
 - ii. Stratigraphy
 - iii. Structural Geology
 - iv. Geophysics
 - v. Subsurface Geologic Model

5. Piezometry and Hydraulic Parameters
 - i. Comprehensive Inventory of Wells (and Diversions?)
 - ii. Historic Reconstruction of Groundwater Pumping
 - iii. Analysis of the System's Piezometric Behavior
 - iv. Pump Tests
 - v. Definition and Interpretation of Subsurface Hydraulic Parameters
 - vi. Characteristics of Regional, Intermediate and Local Flow Systems
6. Hydrogeology
 - i. Hydrostratigraphic Units
 - ii. Hydrologic Basement
 - iii. Definition of the Aquifer System
7. Hydrogeochemistry
 - i. Hydrogeochemical Sampling
 - ii. Water Quality
 - iii. Determination of Dominant Water Types
 - iv. Distribution of Major Ions
8. Conceptual Model of Hydrodynamic Behavior
 - i. Geometry of the Groundwater System
 - ii. Hydraulic Parameters of Hydrostratigraphic Units
 - iii. Definition of Regional, Intermediate and Local Flow Systems
9. Conclusions and Recommendations

Summary of Activities Completed:

- All nine chapters of the Draft Transboundary Aquifer Assessment Report for the San Pedro Aquifer were written in the Spanish language by the USGS and the University of Arizona Water Resources Research Center. The US project partners shared the draft chapters with the University of Sonora for their review during January-March 2013. Binational comments were being integrated by the end of the reporting period.
- Chapters 1, 2, 3, 4 and 7 of the Draft Transboundary Aquifer Assessment Report for the Santa Cruz Aquifer were written in the Spanish language by the USGS and the University of Arizona Water Resources Research Center. The US project partners shared these chapters with the University of Sonora for their review during March-May 2013. Remaining chapters were under development at the time of writing with planned delivery to the Mexican partners by June 2013.
- Project participants from the UA WRRC and the UA Udall Center also contributed to the development of a 5-year report to the U.S. Congress regarding the TAAP. The USGS-issued Open-File Report, published in March 2013, is titled "Five-Year Interim Report of the United States-Mexico Transboundary Aquifer Assessment Program: 2007-2012." The report can be viewed here: <http://pubs.usgs.gov/of/2013/1059/>
- (for a complete list of TAAP publications and other output, see Annex A)

D. Improved linkages with international best practices (via ISARM)

Activity description (2012-13 work plan): Dr. Sharon Megdal and Dr. Chris Scott remained engaged with global and regional (Americas) ISARM initiatives. The Arizona-Sonora effort participates as a case study so as to provide other ISARM participants with information on TAAP as well as learning from other shared resource scenarios.

Summary of Activities Completed:

Dr. Sharon Megdal has engaged stakeholders and representatives of the Internationally Shared Aquifer Resource Management (ISARM) Programme of UNESCO, based in Paris, France. ISARM also maintains regional focus areas, in particular ISARM-Americas (centered in Montevideo, Uruguay), of which TAAP-A/S is recognized as a case study. Dr. Megdal has made presentations in Europe, the Middle East and South America at a variety of ISARM-related meetings and conferences detailing the particular issues related to the binational Santa Cruz and San Pedro aquifers as well as the role of TAAP-A/S in respect to bi-national cooperation related to hydrological assessment of the shared aquifer resources.

A variety of details make TAAP-A/S a unique initiative on the global level, namely the importance of groundwater as supply for potable water, growth rates of urban areas as well as the evolving roles of agriculture and mining/industry in the shared aquifer regions, and also the different governance strategies employed within the US and Mexico in respect to water resources. A main focus of Dr. Megdal's ISARM-related work has been to better understand the organizational asymmetries between water resource assessment and management agencies in the United States and Mexico. The degree of centralization as well as regulation and oversight is unique between the two nations, as well as the existence of the binationally coordinated International Boundary and Water Commission, which has a long history of coordinating resolutions related to the international border and shared waters of the U.S. and Mexico.

TAAP-A/S team members have supported further engagement between representatives of the US Geological Survey and the Mexican National Water Commission, as both agencies provide national representatives to the ISARM-Americas section of the global ISARM Programme. The communication medium of ISARM-Americas provides an excellent opportunity to share and learn from regional counterparts regarding common experiences. In the case of the US and Mexico, the shared border region contains many issues that would benefit from a binational perspective, in which ISARM-Americas may provide a medium in which to develop such a discussion.

Presentations:

Binational Assessment of the Santa Cruz and San Pedro Aquifers: Update of Arizona-Sonora collaboration under the Transboundary Aquifer Assessment Program (TAAP)

By James Callegary, Christopher Scott, Sharon Megdal and Plácido dos Santos. Presented at the Arizona-Mexico Commission Plenary Session - Water and Environment Committees, Tucson, Arizona; June 8, 2012

http://wrrc.arizona.edu/sites/wrrc.arizona.edu/files/pdfs/TAAP_Az-Mex_Commission_June_2012.pdf

The U.S.-Mexico Transboundary Aquifer Assessment Program (TAAP): Focus on the Arizona-Sonora collaboration. The Binational Assessment of the Santa Cruz and San Pedro Aquifers

By Plácido dos Santos. Presented at Binational Border Water Resources Summit: Past, Present and Future. Ciudad Juarez, Chihuahua, Mexico and El Paso, Texas, USA; September 28-29, 2012.

http://wrrc.arizona.edu/sites/wrrc.arizona.edu/files/pdfs/TAAP_Border%20Summit_Sep_2012%20Bilingual_2012_09_24.pdf

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Improving Hydrologic Investigations through Multi-Model Analysis and Discriminatory Data Collection

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Improving Hydrologic Investigations through Multi-Model Analysis and Discriminatory Data Collection

Interim Progress Report, May 2013

Problem Statement and Research Objective

Practicing hydrogeologists are called upon to make specific predictions about future hydrologic conditions that will form the basis for social, economic, and political decisions. The major challenges to accurate hydrologic prediction are: 1) capturing the inherent complexity of hydrogeologic systems in models; and 2) acquiring sufficient informative data to characterize the critical hydrologic processes. Commonly, these modeling and measurement bottlenecks are seen as two interacting, yet separate, aspects of hydrologic science. We propose a novel approach that combines cutting edge tools in hydrologic modeling with a new approach to monitoring network design that addresses both of these fundamental limitations jointly. Specifically, ***we propose to test whether multi-model analysis combined with a discriminatory approach to data collection leads to the selection of more informative hydrogeologic measurement and monitoring networks***. Based on our findings, we will develop a stand-alone tool that can interface with readily available hydrogeologic software to implement Multi-Model Analysis with Discriminatory Data Collection (MMA-DDC).

Methodology

Our current efforts in the development and application of MMA-DDC to hydrologic includes several ongoing, concurrent efforts:

- Developing statistically robust theoretical underpinnings for MMA-DDC
- Implementing the computational procedure for MMA-DDC in modular computer code
- Undertaking a comprehensive literature review to develop a library of mathematical functions suitable for calculating cost functions
- Applying MMA-DDC analysis in several scenarios representative of water resources investigations common to multiple states
 - Optimal monitoring network design for vadose zone contaminant transport
 - Monitoring the effects of groundwater conservation in riparian areas

In the synopsis here, we focus primarily on the first of these four efforts; however, we also note that the second effort – implementing MMA-DDC in modular computer code – is currently in an advanced stage of completion, including adaptation to the applied examples described under effort #4.

Conceptual underpinnings of MMA-DDC

Conceptual development of hydrologic models entails stating hypotheses about the structure, processes, property values, and boundaries of hydrologic systems based on available

information. These hypotheses are embodied in a set of hydrologic models, each capable of making predictions in both space and time. The structure of MMA-DDC is summarized in figure 1. All available information about boundary and initial conditions, parameter values, and process conceptualization is used to develop an ensemble of plausible models. Each model in the ensemble calculates simulated values \hat{Y} for the hydrologic system of interest. These model-simulated values are first divided into calculations of previous and future states and fluxes. Simulated values at and before the present time, τ , are used to assess the relative

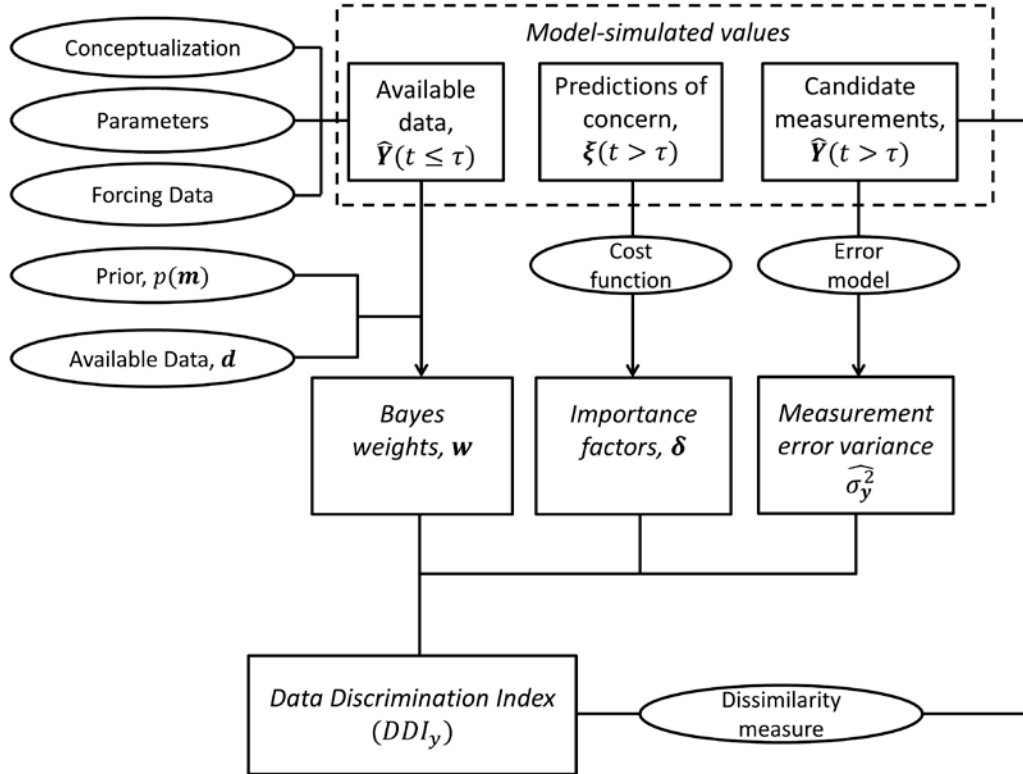


Figure 1. Schematic illustration for calculating the Data Discrimination Index (DDI_y) for a given candidate measurement.

likelihoods of the models in the ensemble. Calculated future values ($t > \tau$) are further subdivided. Some of these future calculations are considered for future data collection and are referred to as *candidate measurements*. Other future calculations are used for decision support and are referred to as *predictions of concern*, ξ . Any of these model-simulated values may be processed through secondary models before they are used. For example, calculations of previous states or fluxes at candidate measurement points can be processed using instrument response models for comparison with geophysical measurements (Hinnell et al., 2010). Similarly, calculations of future states and fluxes can be interpreted with secondary models and cost functions to assess environmental impacts and associated costs. As detailed below, MMA-DDC is designed to combine model likelihoods expressed as Bayes weights, model importance factors

calculated with cost functions, and measurement error variance (with consideration of the expected value of the measurement) to prioritize candidate measurements for collection.

Derivation of the Data Discrimination Index

Consider N models, developed to explain and make predictions of some hydrologic phenomena. We assume that every effort has been made to consider a broad range of possible model structures, thereby fully capturing the uncertainty in model conceptualization, parameterization, and forcing inputs. We wish to use the ensemble of models to make specific predictions of interest and to prioritize future data collection efforts. We consider M candidate measurements and index them based upon measurement type, location, and time. Each candidate measurement will have a vector of N model-simulated values, one corresponding to each model in the ensemble, and referred to as $\widehat{\mathbf{y}}_j$. In addition to the candidate measurements, we consider C predictions of interest for economic, social, or environmental reasons, $\boldsymbol{\xi}$. These predictions of interest, $\boldsymbol{\xi}$, populate an $N \times C$ matrix of values. Some predictions of interest may be directly useful for decision support; for example, predicted changes in streamflow or drawdown surrounding a well. Other predictions of interest may require additional transformation to be used for decision support; for example, exposure time above a regulatory limit may require analysis of the solute concentration time series and may vary by location and species of interest.

Model likelihoods

We use the relative likelihood assigned to each model to weight corresponding simulated values for the candidate observations. The value for the j th candidate measurement simulated by the k th model m_k , will be referred to as $\widehat{y}_{j,k}$. The observed value for this candidate measurement, if selected, will be referred to as y_j . The uncertainty in $\widehat{\mathbf{y}}_j$ is characterized by the probability density function $g(\widehat{\mathbf{y}}_j)$. An appropriate formulation for $g(\widehat{\mathbf{y}}_j)$ is a marginal distribution, summing over all N models:

$$g(\widehat{\mathbf{y}}_j) = \sum_{k=1}^N p(\widehat{y}_{j,k} | m_k) p(m_k) \quad (1)$$

The product inside the summation in equation (1) is the probability that the simulated value, $\widehat{y}_{j,k}$, of the k th model, is correct. The first term on the right hand side of equation (1) is the conditional probability of the k th simulated value, $\widehat{y}_{j,k}$, given that the k th model is correct. The second term on the right hand side of the equation is the probability that the k th model is correct. In the absence of data, $p(m_k)$ is simply the user-specified prior probability. As data become available, then $p(m_k)$ is calculated as the posterior probability of the k th model using Bayes' law:

$$p(m_k | \mathbf{d}) = \frac{p(\mathbf{d} | m_k) p(m_k)}{p(\mathbf{d})} \quad (2)$$

The terms on the right hand side of equation (2) are $\mathcal{L}(m_k | \mathbf{d}) \equiv p(\mathbf{d} | m_k)$, where $\mathcal{L}(m_k | \mathbf{d})$ is the likelihood, $p(m_k)$ is the prior, $p(\mathbf{d})$ is the evidence, and \mathbf{d} is a vector of existing data. The likelihood and the prior vary across the model ensemble, as discussed below. The evidence

depends only upon the available data and serves as a normalizing constant. We can omit $p(\mathbf{d})$ at this point and re-write equation (2):

$$p(m_k|\mathbf{d}) \propto p(m_k)\mathcal{L}(m_k|\mathbf{d}) \quad (3)$$

It is difficult to define a formal likelihood function that mimics exactly the residual distribution in the presence of model and forcing data error (Beven, 2006). Therefore, it is commonly assumed that the residuals are independent and follow a Gaussian distribution. We recognize that many formal and informal methods are available for determining Bayes weights; for example, it would also be possible to use different formal likelihood functions accounting for non-Gaussian and correlated error distributions (e.g. Schoups and Vrugt, 2010). Less formal likelihood functions are also possible, and are discussed in more detail by Smith *et. al.* (2008). The general formulation of the Data Discrimination Index (DDI) allows for flexibility in the selection of model likelihood functions.

After evaluating $p(m_k|\mathbf{d})$ using equations (3) and (4), we next use a normalizing procedure to compute the Bayes' weights:

$$w_k = \frac{p(m_k|\mathbf{d})}{\sum_l^N p(m_l|\mathbf{d})} \quad (4)$$

The quantity w_k on the left hand side of equation (4) is the Bayes' weight, and provides a measure of belief in the k^{th} model. Equation (4) ensures that w_k sums to one over the model ensemble. We then use the Bayes' weights to evaluate $g(\widehat{\mathbf{y}}_j)$, in equation 1:

$$g(\widehat{\mathbf{y}}_j) = \sum_{k=1}^N w_k p(\widehat{y}_{j,k}|m_k) \quad (5)$$

As formulated above, the ensemble of N models includes only models that differ in their underlying concept and model structure; for example, distribution of geologic units, or selection of important hydrologic processes. For each model, specific predictions vary corresponding to the distribution of model inputs and parameters. In approaches based on either regression or mechanistic models, it is common to use the conditional probability in equation (5) to account for parameter uncertainty. For example, we might consider three conceptual models, each of which has ten parameterization schemes. In this case, the conditional probability would be integrated over all ten possible parameterization schemes for each of the three members in the model ensemble. MMA-DDC takes a different approach to specifying the conditional probability in equation (5) by considering each combination of model conceptualization, parameterization, and forcing inputs as a unique member of the model ensemble. We contend that this approach avoids the common confusion of inference and diagnosis of conceptual and parameter uncertainty (Doherty and Christensen, 2011) and allows for a more objective analysis of uncertainties arising from interactions among model inputs, conceptualizations, and parameterizations. With this approach, the total number of simulated values for each candidate measurement is, by definition, equal to the number of models, N . Therefore, the conditional probability in equation (1) may be written as,

$$p(\widehat{y}_{j,k}|m_k) = 1 \quad (6)$$

By combining equations (5) and (6), we define the probability for a given value $\widehat{y}_{j,k}$ of the j th candidate measurement as the Bayes' weight of the k th model.

The MMA-DDC measurement selection process requires the definition of a Data Discrimination Index (DDI) that quantifies the dissimilarity among the predicted values of candidate measurements among the models in the ensemble. The DDI values are used to rank and select from among the candidate measurements. We represent the dissimilarity of model-simulated values for the j th candidate measurement using the standard deviation as a measure of statistical dispersion:

$$DDI_j = \sigma_{\widehat{y}_j} = \sqrt{\sum_{k=1}^N p(\widehat{y}_{j,k}) (\widehat{y}_{j,k} - \bar{\widehat{y}}_j)^2} \quad (7)$$

where $\widehat{y}_{j,k}$ is the model-simulated value, $p(\widehat{y}_{j,k})$ is the probability associated with simulated value $\widehat{y}_{j,k}$, and $\bar{\widehat{y}}_j$ is the mean value of \widehat{y}_j over all N models in the ensemble. Measures of statistical dispersion other than the standard deviation may also be used at this stage in the analysis with appropriate rewriting of equation (7), if so desired. In the absence of data, $p(\widehat{y}_{j,k})$ is the user-specified prior. If data are available, $p(\widehat{y}_{j,k})$ is set equal to the Bayes weight of the k th model w_k , calculated using the available data. Equation (7) is then evaluated by substituting the summand from the marginal distribution in equation (5) for $p(\widehat{y}_{j,k})$, resulting in:

$$DDI_j = \sqrt{\sum_{k=1}^N [p(\widehat{y}_{j,k} | m_k) w_k (\widehat{y}_{j,k} - \bar{\widehat{y}}_j)^2]} \quad (8)$$

Equation (8) defines the standard deviation of ensemble-simulated values representing the candidate measurement y_j . That is, the Data Discrimination Index for the j th candidate measurement depends upon both the distribution of \mathbf{w} and $\widehat{\mathbf{y}}_j$ over the ensemble.

2.4 Model importance

Formulating Bayes' weights to determine model likelihoods lays the groundwork for value-of-data analysis in a multiple model context. Measurement selection in MMA-DDC rests on the fundamental premise that measurements performed at times and locations for which model-simulated values are most dissimilar reduces critical uncertainties in hydrologic model predictions, thereby providing data that are best suited for decision support. Stated another way, there is little or no expected value in collecting an observation that is predicted to be very similar by all of the models in the ensemble. As discussed below, we simultaneously consider the importance of models in the ensemble based on the expected value (or cost) of their predictions. In this way, *MMA-DDC is designed to identify the data that are most likely to reduce prediction uncertainties that are most important for decision support.*

For the purposes of management and decision-making, the prediction uncertainties most important for decision support are those that lead to the greatest cost (or lowest value) due to uncertainties in predictions of interest that relate to social, ecological, or economic outcomes. We wish to focus our data collection efforts on acquiring observations that are most like to reduce these critical uncertainties in model predictions. Our approach is based on the standard definition of expected value, or utility, first presented by Daniel Bernoulli (Bernoulli, 1738). This states that the expected value is the sum of the product of the likelihood and cost (or value) of each outcome over all possible outcomes. The models in the ensemble and associated cost models can provide both of these measures, allowing us to calculate the expected cost (or value) for any predicted future condition. Some portion of this expected utility is due to models with relatively low likelihood, but predictions of interest that differ in important ways from the maximum likelihood predictions. Another portion of the expected utility is due to models with predictions of interest that are equal to or only slightly different from the expected value, but that have high likelihoods.

To prioritize both of these cases, we define an importance factor for each model as:

$$\delta_k = \boldsymbol{\omega}^T f(\boldsymbol{\xi}_k) \quad (9)$$

In equation (9), $\boldsymbol{\omega}^T$ is the transpose of a weighting vector used to assign relative importance coefficients to the costs associated with $\boldsymbol{\xi}_k$. Those costs are calculated by the cost function, $f(\cdot)$. The cost function for the k th model depends exclusively upon the predictions of concern, $\boldsymbol{\xi}_k$. We are currently working towards the development of a cost function library, which will provide the user with options for selecting common mathematical forms for economic cost functions for use in this analysis. Examples of cost functions are shown in figure 2.

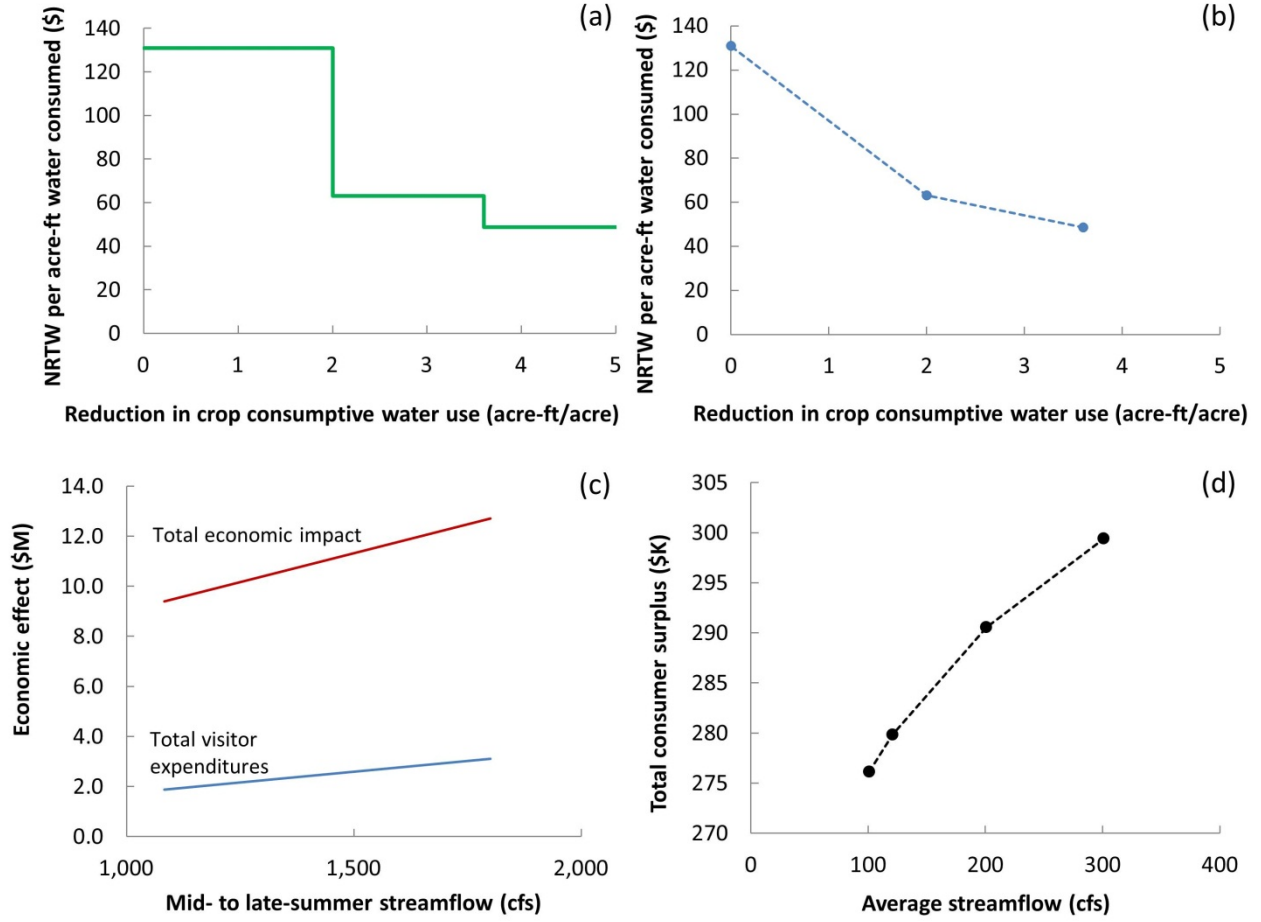


Figure 2. Examples of cost functions suitable for use in DIRECT. Change in Net Returns to Water (NRTW) from (a) substitution of water-efficient crops, and (b) incremental changes in crop acreage and irrigation intensity in the Lower Colorado River Basin. (c) Predicted visitor expenditures and total economic impact at different streamflow levels on the Upper Rio Grande, New Mexico, (d) Total consumer surplus at different streamflow levels on the Feather River, California.

Each model is then weighted by its corresponding importance factor:

$$DDI_j = \left(\overline{\sigma_{\hat{y}_j}^2} \right)^{-1} \sqrt{\sum_{k=1}^N \left[p(\hat{y}_{j,k} | m_k) w_k \delta_k (\hat{y}_{j,k} - \bar{\hat{y}}_j)^2 \right]} \quad (10)$$

In certain stakeholder negotiation scenarios, it is very difficult to determine objectively the weighting vector ω ; instead, it may be better to consider the different predictions of concern in a multicriteria framework (Hajkowicz and Collins, 2007). To satisfy this concern, the weighting vector ω would be omitted from equation (9), resulting in a vector δ_k containing costs associated with each prediction of concern in ξ_k . After calculating N vectors δ_k , the entries from each δ_k would then be used to compute a set of distinct DDI values for each prediction of concern for each candidate measurement.

2.5 Measurement error

The set of candidate measurements may include multiple measurement types. Therefore, we need to account explicitly for the expected observational error of each measurement to allow for quantitative intercomparison among the candidate observations. It is often assumed that observational error, ε , follows a Gaussian distribution; that is,

$$\varepsilon \sim N(0, \sigma_{y_j}^2) \quad (11)$$

MMA-DDC is not restricted to this assumption; however, for simplicity, we adopt this assumption for the examples presented herein. We further assume that measurement errors are independent. In equation (11), $\sigma_{y_j}^2$ is the measurement error variance, and depends on the nature of errors arising from particular measurement techniques rather than conceptual, parameter, and input uncertainties pertaining to the hydrologic system. The measurement error variance may be either homoscedastic or heteroscedastic. For the heteroscedastic case, the value of $\sigma_{y_j}^2$ depends on the numerical value of the candidate measurement, y_j . In a measurement selection context, $\sigma_{y_j}^2$ is therefore difficult to estimate since the candidate measurement values are, by definition, unknown. It would be possible to estimate $\sigma_{y_j}^2$ using the expected value of y_j if the theoretical distribution on y_j is known; however, this is seldom, if ever, the case. Alternately, we may use the model ensemble to estimate $\sigma_{y_j}^2$ as the expected value of $\sigma_{\widehat{y}_j}^2$, using the probability density function $g(\widehat{y}_j)$:

$$E[\sigma_{y_j}^2] \approx \overline{\sigma_{\widehat{y}_j}^2} = \frac{1}{N} \sum_{k=1}^N g(\widehat{y}_{j,k}) \sigma_{\widehat{y}_{j,k}}^2 \quad (12)$$

Calculating the value of $\sigma_{\widehat{y}_{j,k}}^2$ for a given value $\widehat{y}_{j,k}$ requires a measurement error model for each candidate measurement. In general, the measurement error model would be expected to differ among measurement types. If the measurement errors are expected to be heteroscedastic, definition of the measurement error variance for a particular candidate measurement using equation (12) requires a probability density function $g(\widehat{y}_j)$, and a measurement error model for the candidate measurement. For the more simple homoscedastic case, the measurement error variance would be a user-specified constant. To provide intercomparison among all candidate measurement types, we use the inverse of the estimated measurement error variance, $(\overline{\sigma_{\widehat{y}_j}^2})^{-1}$, to weight the DDI:

$$DDI_j = (\overline{\sigma_{\widehat{y}_j}^2})^{-1} \sqrt{\sum_{k=1}^N [p(\widehat{y}_{j,k}|m_k) w_k (\widehat{y}_{j,k} - \bar{y}_j)^2]} \quad (13)$$

The purpose of this weighting is to account for data points that may differ in quality. That is, some candidate measurements are potentially informative, but are less useful due to relatively

high measurement error. This inverse weighting procedure is designed to screen out those less useful candidate measurements. Stated another way, we seek to normalize all measurements by their expected noise so that all observations can be compared in a single, unitless objective function in terms of their signal to noise ratio.

The unitless DDI is calculated for each candidate measurement. In this preliminary investigation of MMA-DDC, we examine the simplest procedure: selecting candidate measurements with the highest DDI as the most discriminatory dataset. We further assume that the structure of the data collection efforts (e.g. number of measurements at each measurement time) is constrained. For cases in which few proposed observations are available, it is possible to perform this selection by inspection. If there are many proposed measurements encompassing significant variability in the location, timing and measurement type, then optimization is required to identify the most discriminatory dataset.

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Iodinated Disinfection By-product Formation from Water Reuse Practices

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Descriptors:	None
Principal Investigators:	Shane Snyder

Publications

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Disinfection By-product Formation from Water Reuse Practices
WRRI/USGS 104(b) Program Award (Project 2011AZ450B)

Shane A. Snyder

Problem and Research Objectives

Expanding water demands have put increasing pressure on water agencies, city officials, and scientists to develop innovative ideas to seek alternative renewable water supplies. One alternative source of water which is reliable and local is wastewater discharged from Reclaimed water is a viable option. This recycled water is treated to various extents depending on intended use. Historically, recycled water was used primarily for land application, either for irrigation or to recharge underlying groundwater through percolation. If a drinking water treatment plant draws water from the same aquifer, this is called indirect potable reuse (IPR). As an alternative, generally due to limits in land area and/or geology, recycled water is treated with advanced processes and injected into an aquifer. However, there is recent interest in eliminating this environmental buffer by connecting the highly treated recycled water directly to a drinking water system. These systems are known as direct potable reuse (DPR) and two such systems have been constructed in the USA (one in New Mexico and one in Texas) and several others are in planning. It is anticipated that potable will become an increasingly important part of water management, especially in the arid Southwest where groundwater is often withdrawn faster than it is replenished by the natural hydrological cycle. Therefore, the significant growth in potable reuse is expected in Arizona, and throughout the Southwest USA, in the near future.

However, there are some notable concerns regarding potable water reuse (PWR). Public acceptance of PWR is challenging, as it is difficult to convince citizens that drinking “treated” wastewater is safe. Citizens should be reassured that utilities are required to ensure that sufficiently low numbers of bacteria leave in the effluent recharge, and that the water is devoid of chemicals at levels of risk to public health. This is accomplished via sufficient disinfection and/or advanced treatment and/or prolonged aquifer percolation time. While utilities emphasize water treatment for harmful biological entities, they sometimes inadvertently create transformation products from trace organic compounds (TOCs) and from natural organic matter (NOM). Therefore, when ozone, chlorine, UV, and/or chloramines are utilized for disinfection and/or contaminant oxidation, disinfection by-products (DBPs) may form from reactions with organic substances. Since wastewater contains high iodide and bromide concentrations compared to most “natural” waters, PWR can generate unique DBPs and at concentrations atypical for a non-impacted site.

The majority of disinfection byproducts formed during water treatment remains unknown (Krasner, Weinberg et al. 2006). Iodinated and nitrogenous DBPs (IDBs and NDBs, respectively) are, by far, the most toxic group of transformation products formed during oxidative water treatment processes (Plewa, Muellner et al. 2008; Richardson, Fasano et al. 2008). Mammalian cell studies have shown that iodoacetic acid is 3.2 and 287.5 times

more cytotoxic in Chinese hamster ovary cells than bromoacetic acid and chloroacetic acid, respectively; and iodoacetic acid is 2.0 and 47.2 times more genotoxic in Chinese hamster ovary cells than bromoacetic acid and chloroacetic acid, respectively (Plewa, Muellner et al. 2008). A commonly detected NDBP is nitrosodimethylamine (NDMA), which has a calculated cancer risk as low as 0.7 ng/L (Mitch, Oelker et al. 2005). However, despite their higher toxicity, IDBPs and NDBPs are not yet regulated. The lack of federal regulation is due in part to limited occurrence data since reliable and sensitive analytical methodologies are not yet commonly available. However, recent advances in analytical technology coupled with commercial availability of purified reference standards are allowing further investigation into this new generation of DBPs. Since wastewater is known to contain elevated levels of iodine and organic nitrogen, the oxidative technologies commonly employed to purify to potable standards can result in elevated levels of IDBPs and NDBPs as compared to a non-impacted potable source water.

The primary objective of this study was to determine the attenuation of TOrC using ozone and the potential formation IDBPs and NDMA in wastewaters that are, or maybe, utilized for potable reuse. In order to achieve this objective, we developed and implemented a novel method for characterizing IDBPs and evaluated the formation potential in actual waters. We further evaluated the formation and fate of NDMA in water under various treatment scenarios.

Methodology

Sample Collection and Preservation

Samples were collected by Tucson Water and Pima County staff in pre-cleaned five gallon polypropylene carboys. The two wastewater samples (Roger Rd and Ina Rd) were quenched within four hours of receipt in the lab with 20 mg/L of sodium thiosulfate and the free chlorine was measured using a Hach DPD kit. Groundwater samples did not have any residual chlorine and thus were not quenched. All samples were stored at 4 °C till the time of analysis.

Ozonation

Water samples were ozonated at three different doses within five days of collection. A concentrated ozone stock was prepared by bubbling gaseous ozone with a diffuser into ultra-pure water in a specialized liquid-jacketed vessel. The vessel was cooled to 1°C with ethylene glycol and a recirculating chiller. The resulting ozone stock solution was tested for residual ozone concentration and found to be >40 mg/L. An aliquot of ozone stock solution was then placed into the ozone reaction vessel containing the sample to achieve the desired ozone concentration. The ozone residual was tested using the Indigo method every 30 seconds for the first 2 minutes followed by every minute from 3-10 minutes and every 2 minutes from 10-20 minutes.

The above procedure was performed again to obtain the samples for analysis of nitrosodimethylamine (NDMA), trace organic compounds (TOrCs), disinfection byproducts, bromide (Br^-) and bromate (BrO_3^-). Ozone residual for these samples was

quenched and post-ozonated water remained at ambient temperature for six hours to ensure the ozone was completely consumed.

Groundwater samples were chlorinated and chloraminated to achieve a one ppm residual with a contact time of one day to determine DBP formation potential. The preparation of the chlorine and chloramine (as monochloramine) stocks is described below.

Chlorine Stock Solution

Chlorine stock solution was prepared by diluting a sodium hypochlorite solution (6% available chlorine). Commercial sodium hypochlorite solution was initially diluted and verified by UV spectrometry at 292nm. A molar absorption coefficient of $362 \text{ Lmol}^{-1}\text{cm}^{-1}$ was used to calculate the measured concentration of the commercial solution. Based on the calculated concentration, sodium hypochlorite solution was added to deionized water to create a desired stock solution concentration.

Monochloramine Stock Solution

Preformed monochloramine stock solution was prepared by combining sodium hypochlorite to ammonium chloride. To create monochloramine, deionized water was put in a volumetric flask and placed on a stir plate. Sodium hydroxide and ammonium chloride at 10g/L were then added. Sodium hypochlorite was then slowly added (drop by drop) to create a N:Cl ratio of 1:1.4. To ensure proper formation, solution was well stirred during the addition of sodium hypochlorite. The solution was then covered with foil to avoid degradation by light.

To confirm the concentration, the solution was verified by UV spectrometry. Absorbance readings at 245 nm and 295nm for NH_2Cl and NHCl_2 , respectively, were then used to determine exact stock solution concentration.

Chlorination/Chloramination Procedure

- 1) Prepare bottles (# of bottles = # of samples + blank(s))
- 2) Prepare chlorine stock solution at 1.4mM.
- 3) Prepare monochloramine stock solution at 1.4mM.
- 4) Prepare carbonate buffer at 500mM.
- 5) Prepare a diluted hydrochloric acid solution for pH adjustments (1M).
- 6) Fill bottles with sample water.
- 7) Calculate the dose volume for monochloramine, chlorine, and carbonate buffer based on total volume and desired dose concentration. Remove sample volume based on disinfectant and buffer addition. This step is necessary to ensure final dose concentration is accurate. For example, if 100mL sample volumes, stock solutions at 1.4mM, and a buffer at 500mM were used, 1mL and 0.8mL was removed for disinfectant and buffer addition, respectively.
- 8) Add carbonate buffer.
- 9) Add chlorine or monochloramine.
- 10) Record exact time of dosing.
- 11) Check for pH and add HCl to obtain a pH of 8.
- 12) Cap and store in a dark location.

Dissolved Organic Carbon

A Shimadzu TOC-L CSH Total Organic Carbon Analyzer was used to determine the dissolved organic carbon (DOC) of the wastewater samples. The method followed is very similar to standard method 5310 (APHA 2012). This instrument incinerates the samples at approximate 680 °C to convert total carbon components to carbon dioxide. The resulting gas is cooled, dehydrated and delivered to a non-dispersive infrared (NDIR) gas analyzer to detect the amount of carbon dioxide. The flow line was washed twice before the first injection of each sample. Sparge gas flow was set as 80 mL/min with a sparge time of 1.5 minute. The injection volume was 50 µL.

Stock solutions of TOC were prepared at 1000 mg/L in Milli-Q water and stored at 4 °C. Calibration standard solutions ranging from 1 to 20 mg/L were prepared from the stock solutions. Calibration curves were used only if the linearity was higher than 0.99 and each calibration point had accuracy between 80% and 120%, otherwise the calibration curve was prepared again and reanalyzed.

For DOC analysis, the samples are filtered with a 0.45 µm glass fiber filter before acidification and analysis on the instrument. While TOC samples are not filtered.

Approximately 15 mL of the samples were transferred into 20 mL glass vials for DOC analysis. Then they were acidified to pH 3 or lower using hydrochloric acid (35%). pH test papers were used to determine the final pH. To avoid contamination, all the glassware was pre-furnaced at 550 °C for 5 hours.

To ensure the precision of the measurements, every sample including calibration standards and lab blanks was injected five times, and the average of the three closest measurements was reported. In addition, a quality control sample of known concentration was analyzed with every 10 samples to monitor instrumental accuracy and drift.

Nitrate/Nitrite

Nitrate and nitrite was analyzed using a Dionex ICS-1000 with an AS-22 column set (with AS-22 guard) Ion Chromatograph (IC).

Trihalomethanes (THMs)

The extraction procedure was based on US EPA Method 555.1. A 10 mL sample volume was extracted with 10 mL of methyl-tert-butyl-ether (MTBE). Four grams of sodium sulfate was added for a “salting out” effect and sample vials were vigorously shaken until sodium sulfate was fully dissolved. MTBE extracts were collected and placed into a 2 mL autosampler vial. For quality control purposes, a laboratory reagent blank and laboratory fortified blank was included with each extraction batch. Each sample was extracted in duplicate with 1,2,3-trichloropropane added as a surrogate.

MTBE extracts were analyzed with an Agilent 7890A Gas Chromatograph equipped with a linearized electron capture detector (ECD), fused silica capillary column, and split/splitless injector. The GC system was equipped with an Agilent HP-5 column (30 m x 0.25 mm x 0.25 µm).

N-Nitrosodimethylamine (NDMA)

Samples were filtered through 0.7 µm glass fiber filters upon receipt and stored at 4 °C until extraction. The protocol for extraction closely followed that of EPA 521. EnviroCarb coconut charcoal cartridges were used for the solid phase extraction (SPE). Nitrosamines are extracted by passing a 500 ml aliquot sample (spiked with NDMA-d6 as a surrogate) through the SPE cartridge containing 2 g of 80-120 mesh coconut charcoal. Cartridges are conditioned prior to extract by sequential addition of 3 ml methylene chloride, 3 ml methanol (repeated 3 times), followed by 3 ml HPLC grade water, repeated 5 times. Water samples were loaded onto the cartridge at a rate of 10 ml/min. Analytes are eluted from the cartridge using 10 ml of methylene chloride. Residual water was eliminated from sample extract by passing through 5-7 g of anhydrous sodium sulfate. Eluent was then concentrated under a gentle stream of nitrogen to 0.9 ml. Prior to immediate analysis, 20 µl of 500ug/ml NDPA-d14 internal standard is added to the extract.

Nitrosamine analysis was conducted using an Agilent 7000 triple quadrupole mass spectrometer coupled to an Agilent 7890 gas chromatograph. All gases used were ultra-high purity or equivalent. A DB-WAX ETR capillary column from J&W Scientific (30m x 0.25mm ID x 0.25µm) was employed for gas chromatographic separation with the following oven temperature program: 40 °C (3 minute hold), heating to 110 °C at 10 °C/min, ramping at 15 °C/min to 200 °C, with a final progression of 40 °C/min to 240 °C. The column was operated at a constant helium flow rate of 1.25 ml/min with injector in splitless mode and held at 200 °C. The MS interface was held at 240 °C, while the source temperature was 200 °C and both quadrupoles maintained at 150 °C. The mass spectrometer was operated in positive chemical ionization mode with nitrogen collision cell gas at 1.5 ml/min, helium quench gas at 2.25 ml/min, and using 20% ammonia as the reagent gas. Analytes were detected in multiple reaction monitoring mode (MRM).

Trace Organic Compounds (TOrcs)

Samples were fortified with a surrogate standard stock to obtain a final concentration of 200 ng/L. Samples were subsequently filtered through 0.2 µm PES syringe filters from GE Whatman. Two sets of samples were prepared: a 1.5 ml sample and a sample diluted 5x with ultrapure water (300µL sample + 1200 µL water) so as to obtain concentrations of all analytes within the linear range of calibration curve. Calibration standards were freshly prepared from a 1 mg/L stock of all target analytes.

TOrc analysis was performed using online solid-phase extraction coupled to an ultra-high performance liquid chromatography-tandem mass spectrometer (UHPLC-MS/MS). This UHPLC-MS/MS method utilizes a polymeric solid phase extraction cartridge that is attached online to an Agilent 1290 Infinity LC, which in turn is coupled to an Agilent 6460 LC/MS Triple Quadrupole system. It utilizes simultaneous positive and negative electrospray ionization (ESI) to provide significant time savings. The method uses a dynamic multiple reaction monitoring (DMRM) mode for even more sensitivity and specificity of detection. Further details on compound and instrument optimized parameters have been published elsewhere (Anumol, Mohsin et al. 2013). Data was processed using the Mass Hunter software and samples were quantified using the isotope

dilution method(Vanderford and Snyder 2006). The analysis of 28 TOrCs was performed on all samples as indicated in Table1.

Table 1. Trace Organic Compounds Analyzed

Trace Organic Contaminant	Trace Organic contaminant
Atenolol	DEET
Caffeine	Propylparaben
Benzotriazole	Bisphenol A
Trimethoprim	Testosterone
Primidone	Naproxen
Sulfamethoxazole	PFOA
Meprobamate	Estrone
Diphenhydramine	TCP
Prednisone	Benzophenone
Ditiazem	Ibuprofen
Simazine	Gemfibrozil
Carbamezapine	PFOS
Dexamethasone	Triclocarban
Atrazine	Triclosan

Bromide/Bromate

Sample analysis was performed using an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS) that is interfaced with an Agilent 1260 liquid chromatograph (LC). The ICP-MS is operated in helium collision mode, in order to remove the effects of polyatomic interferences. The speciation of bromide and bromate was performed using a Dionex AG-9 HC/AS-9 HC (4 mm) ion chromatography column eluted using an isocratic 10 mM sodium carbonate (flow rate = 1.0 mL/min) solution over the time course of 25 minutes. During the experiment, ion intensities for both ^{79}Br and ^{81}Br are recorded as a function of time, concentrations in water samples are determined by evaluating areas of peaks and comparing these to the areas obtained for calibration standards.

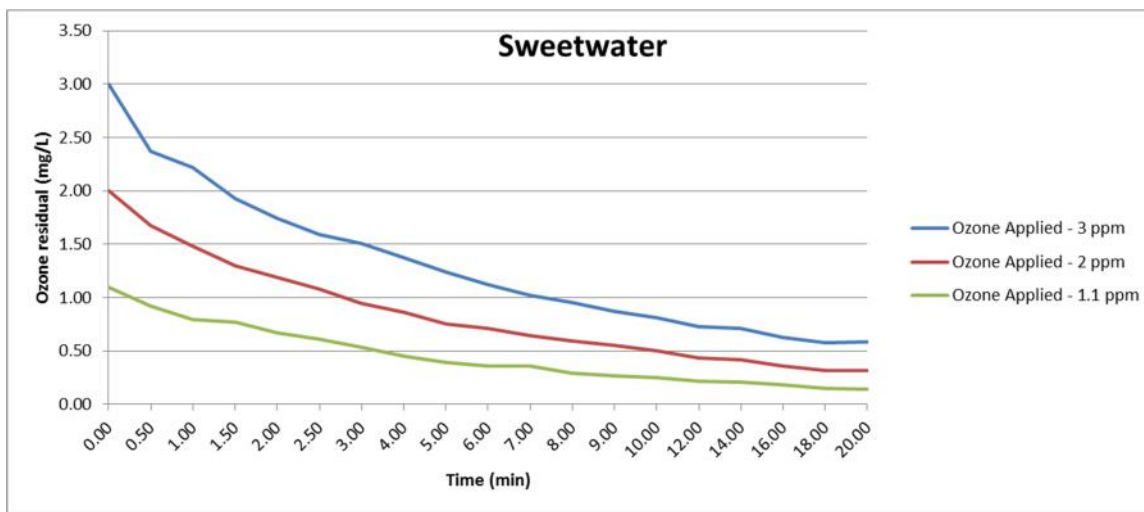
GC-ICP-MS

Samples were split in two, one half was left untreated and the other half was treated with aqueous chloramine. For extraction, 35 mL of these wastewater samples were extracted using 5 mL of MTBE in a modified version of EPA method 551.1. The organic layers were carefully separated and then placed into 2.0 mL amber Agilent GC vials. The organic extracts (1 μL) were then injected into an Agilent 7890A gas chromatograph equipped with 30 m Agilent HP-5 column (320 μm x 0.25 μm) in pulsed splitless injection mode. Oven parameters were 37 $^{\circ}\text{C}$ for 6 minutes, followed by a 10 $^{\circ}\text{C}/\text{min}$ rise up to 260 $^{\circ}\text{C}$ followed by an 11 minute hold time. The heated ICP-MS transfer line and the ICP-MS injector were operated at 200 $^{\circ}\text{C}$. A dilution gas (Ar) flow of 0.39 L/min was used to carry the column outflow through the transfer line. Calibration curves for iodine and bromine were prepared using standards of 1-bromo-4-iodobenzene with concentrations of 0, 1, 2, 5, 10, 25, and 100 ng/mL prepared in MTBE.

Principal Findings and Significance

The Ina Road (IR) effluent DOC was found to be 5.4 mg/L and only exhibited ozone residual at the highest ozone dose applied. The Roger Road (RR) effluent sample had DOC that was extremely high at 10.4 mg/L, which resulted in instantaneous ozone demand greater than all four ozone doses (1, 3, 5, and 7 mg/L). Thus, no ozone residual was detected after the first seconds of application. Conversely, the soil infiltration of Roger Road effluent seems to remove a large amount of DOC as the Sweetwater (SW) sample had DOC of 0.7 mg/L). Thus, ozone applied to SW showed ozone residual at all doses (1, 2, and 3 mg/L) and exhibited relatively slow decay, typical of a low DOC water (Figure 1). Roger Road was also determined to have a high level of nitrite, which consumes ozone at a 1:1 molar rate. Both IR and SW samples had no detectable nitrite. Nitrate at RR was 3.92 mg/L, while IR and SW were 29.5 and 17.7 mg/L, respectively.

Figure 1. Ozone Demand/Decay of Sweetwater Recovery Water



Ozonation of RR and IR effluents produced very low bromate concentrations (Table 2). This is as expected considering the high consumption rate of ozone, which suggests that bromide is unable to react with ozone because of the relatively low rate constant ($k \sim 10^2 \text{ M}^{-1}\text{s}^{-1}$). However, bromate formation was quite high in the SW sample. Interestingly, the bromide reduced almost equivalently indicating that the bromide was converted to bromate on reaction with ozone.

A high concentration of many TORCs was detected in the RR effluent compared to the IR effluent (Table 3). Most of the TORCs are attenuated by infiltration though as the SW sample was found to have only four detectable TORCs. Ozone treatment generally resulted in removal of TORCs but removals were largely based on the rate constant of the contaminant with ozone (Huber, Gobel et al. 2005; Wert, Rosario-Ortiz et al. 2009).

Roger Rd				
Sample	No Ozone	1 ppm	3 ppm	5 ppm
Bromate (ug/L)	BLQ	BLQ	3	2
Bromide (ug/L)	221	209	196	182
Ina Rd				
Sample	No Ozone	1 ppm	3 ppm	5 ppm
Bromate (ug/L)	1	1	1	4
Bromide (ug/L)	176	178	159	148
Sweet water				
Sample	No Ozone	1 ppm	2 ppm	3 ppm
Bromate (ug/L)	BLQ	67	242	394
Bromide (ug/L)	434	283	164	92
BLQ-Below Limit of Quantification				

	Roger Road					Ina Road					Sweet Water			
Sample (Conc. In ng/L)	No Ozone	1 ppm	3 ppm	5 ppm		No Ozone	1 ppm	3 ppm	5 ppm		No Ozone	1 ppm	2 ppm	3 ppm
Atenolol	1800	1670	1610	1260		450	360	310	220		10	BLQ	BLQ	BLQ
Caffeine	3260	2770	2900	2300		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Benzotriazole	6210	5830	2960	2660		2020	2000	1660	1120		BLQ	BLQ	BLQ	BLQ
Trimethoprim	1090	1140	970	700		260	300	200	110		BLQ	BLQ	BLQ	BLQ
Primidone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Sulfamethoxazole	1350	1210	970	770		1430	1050	820	490		BLQ	BLQ	BLQ	BLQ
Meprobamate	650	570	580	480		750	679	576	458		BLQ	BLQ	BLQ	BLQ
Diphenhydramine	1720	1550	910	680		810	590	470	410		BLQ	BLQ	BLQ	BLQ
Prednisone	BLQ	BLQ	BLQ	BLQ		100	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Ditiazem	310	280	190	110		260	140	110	70		90	17	16	15
Simazine	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Carbamazepine	310	240	280	130		390	300	190	100		350	BLQ	BLQ	BLQ
Dexamethasone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Atrazine	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
DEET	400	380	360	300		59	62	50	38		BLQ	BLQ	BLQ	BLQ
Propylparaben	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Bisphenol A	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Testosterone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Naproxen	500	350	450	240		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
PFOA	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Estrone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
TCPP	4000	4300	3600	2350		9500	9500	10000	10000		120	140	90	90
Benzophenone	480	590	430	460		200	170	110	110		190	190	60	70
Ibuprofen	170	160	100	78		79	26	22	17		BLQ	BLQ	BLQ	BLQ
Gemfibrozil	4630	4090	4100	2780		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
PFOS	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Triclocarban	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Triclosan	980	320	100	80		140	34	19	12		BLQ	BLQ	BLQ	BLQ
BLQ: Below Limit of Quantification														

NDMA formation increased in response to ozone dose in the RR sample (Table 4). The effluent NDMA at RR was also higher than the other two samples (IR and SW). The trend in IR is not clear and further studies may be required. The SW sample had an initial increase in NDMA but did not change at higher ozone doses, suggesting that precursors resulting in NDMA formation likely were completely consumed at the initial ozone dose. Additionally, chlorination and chloramination of SW sample did not result in NDMA formation.

Table 4. NDMA Formation Ozonation (ng/L)

Roger Rd			
No Ozone	1 ppm	3 ppm	5 ppm
17	24	28	31
Ina Rd			
No Ozone	1 ppm	3 ppm	5 ppm
9	7	4	7
Sweet water			
No Ozone	1 ppm	2 ppm	3 ppm
BLQ	4	4	4

BLQ-Below Limit of Quantification

The THMs present in all samples were much lower than the current MCL of 80 µg/L. There was a slight increase in TTHMs on ozonation and chlorination of the SW sample (Table 5).

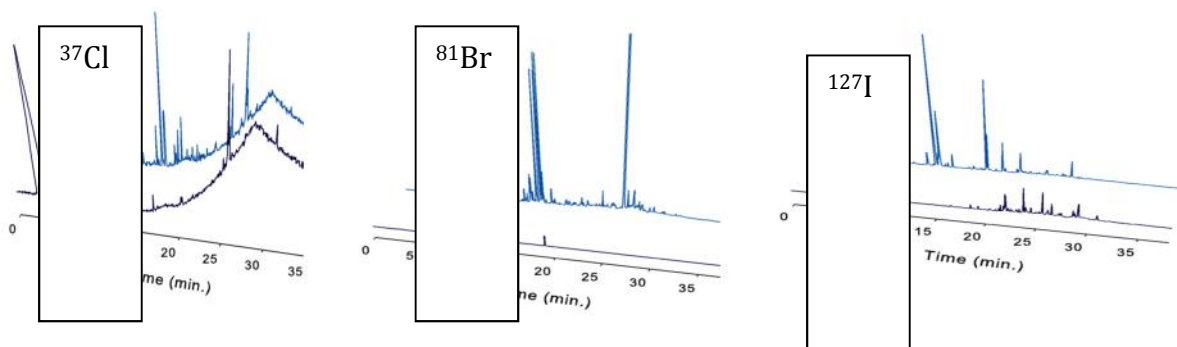
Table 5. Trihalomethane Formation in Sweetwater Sample

Sweetwater					
	Ozone/Chlorine (mg/L)			Ozone/Chloramine	
Compound (Conc. in µg/L)	0/0	1/1	0/1	1/1	0/1
Chloroform	5.8	5.8	5.7	BLQ	BLQ
Dichlorobromomethane	BLQ	9.3	9.0	BLQ	BLQ
Chlorodibromomethane	BLQ	5.3	5.5	BLQ	BLQ
Bromoform	16.1	16.0	15.6	12.5	BLQ
Dichloriodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Dibromiodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Bromochloriodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Chlorodiiodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Bromodiiodomethane	BLQ	BLQ	BLQ	5.3	5.6
Iodoform	BLQ	BLQ	BLQ	BLQ	BLQ
Tribromochloromethane	BLQ	BLQ	BLQ	BLQ	BLQ
Σ T H M	21.9	36.5	35.9	12.5	0.0

Using GC-ICP-MS, the treatment with chloramine leads to an increase in the concentration of chlorinated, brominated, and iodinated species in the extracts (Figure 2).

Our data reveals several interesting facts. First, there are indeed volatile halogenated organics present in wastewaters prior to chloramination, some of these species are resistant to transformation upon treatment while some are consumed (and likely transformed into new halogenated DBPs). Indeed, it is likely that many non-halogenated organics in the untreated wastewaters are converted into new halogenated DBPs, as well.

Figure 2. GC-ICPMS chromatograms obtained from MTBE extracts prepared from a representative wastewater sample before chloramination (purple line) and after chloramination (blue line).



The effects of chloramination is seen most profoundly in terms of the differences between chromatograms for brominated and iodinated DBPs. There are two reinforcing explanations for this, one dealing with the reactivity of bromide and iodide during oxidative treatments, and the higher sensitivity for detection for I and Br in our assays due to their lower ionization potentials (relative to Cl). A brief summary of our results for a few (of many) halogenated organics in two different wastewaters before and after treatment are shown in Table 6. All CCVs conducted at the end of our analysis provided agreement within 10% of the initial bromine and iodine signal responses for our initial calibration.

Table 6. A simplified table revealing the halogen concentrations in a series of halogenated volatile organics present in extracts that have been prepared from wastewaters before and after chloramination.

Compound name	35 Cl-1	35 Cl-2	35 Cl-3	81 Br-1	81 Br-2	127 I-1	127 I-2	127 I-3	127 I-4	127 I-5	127 I-6
Retention Time (min)	15.3	15.8	17.0	15.4	19.0	20.6	25.2	12.2	12.6	20.6	29.0
Sample Name	[Cl], ppb	[Cl], ppb	[Cl], ppb	[Br], ppb	[Br], ppb	[Br], ppb	[Br], ppb	[I], ppb	[I], ppb	[I], ppb	[I], ppb
mtbe BLANK	5.5	6.9	6.2	1.3	0.5	2.4	1.1	0.1	0.3		0.4
Br-I-benzene 1ppb	14.0	4.0	15.8	0.4	0.5	1.3	1.1	0.2	0.2	0.5	0.2
Br-I-benzene 2 ppb	3.6	7.5	3.3	1.5	0.8	1.7	1.0	0.0	0.0	0.8	0.2
Br-I-benzene 5 ppb	17.8	3.5	5.0	0.4	0.1	1.2	0.5	0.2	0.2	2.5	0.5
Br-I-benzene 10 ppb	7.7	13.2	6.0	0.5	0.2	3.0	0.6	0.2	0.3	4.4	0.1
Br-I-benzene 25 ppb	10.6	5.3	5.8	1.3	0.1	7.1	1.6	0.1	0.2	11.9	0.3
Br-I-benzene 100 ppb	8.6	4.1	3.1	0.2	0.2	28.3	0.6	0.1	0.1	44.7	0.5
mtbe BLANK			33.1		2.5		4.2	1.2	0.6		0.6
Sample 1 before	11.8	11.8	56.0	1.1	346.8	3.2	15.6		1.3	4.6	26.0
Sample 1 after	468.7	357.9	69.5	3315.0	293.7		44558.0	169.9	103.4		1.6
Sample 2 before	7.7	11.7	17.0	3.5	3.2		19.0	0.1	0.6	0.7	1.3
Sample 2 after	453.8	261.7	188.1	4819.9	1254.7	1377.7	121428.9	23.5	34.8	18.5	6.6
Sample 3 before	30.7	43.7	33.0	15.4	37.9		100.1	4.1	2.6	1.3	14.8
Sample 3 after	1465.5	130.0	70.9	3388.6	1130.8		126629.7	31.9	103.6	28.5	29.7

Conclusions

This study shows that when local wastewater are ozonated, a great decrease in TOrCs will be observed; however, depending on dose, NDMA formation can be formidable. Conversely, the formation of bromate did not seem significant in wastewaters due to high ozone consumption. NDMA formation was at times significant; however, infiltration seems to have attenuated precursors significantly. The formation of IDBs of known structure were at concentrations far lower than expected. However, the use of GC-ICP-MS demonstrated that a large number of currently unknown IDBPs and BrDBPs are formed during chloramination. This novel data should be more thoroughly explored using QTOF mass spectrometry and in vitro bioassays. Fortunately, the infiltration of RR water clearly improves water quality at nearly all measures and generally increase treatment performance do improvement in DOC, nitrate, and in ToRC concentrations.

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Fate of Emerging Nanoparticle Contaminants during Aquifer Recharge with Treated Wastewater

Basic Information

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Publications

1. Rottman, J., R. Sierra-Alvarez, F. Shadman. 2013. Real-time monitoring of nanoparticle retention in porous media. Environ. Chem. Lett. DOI 10.1007/s10311-012-0381-3.
2. Rottman, J., L. Platt, R. Sierra-Alvarez, F. Shadman. 2013. Removal of TiO₂ nanoparticles by porous media: effect of filtration media and water chemistry. Chem. Eng. J. 217(1):212-220.
3. Rottman, J. J. 2012. Fundamentals and application of porous media filtration for the removal of nanoparticles from industrial wastewater. "PhD Dissertation" , Department of Chemical and Environmental Engineering, College of Engineering, The University of Arizona, Tucson, Arizona, 158 pp.

Fate of Emerging Nanoparticle Contaminants during Aquifer Recharge with Treated Wastewater (Project # 2012AZ476B)

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A. Problem and Research Objectives

A.i) Background

Nanoparticles and their applications. Nanoparticles (NPs) can be defined as particles with at least one dimension less than 100 nm. Nanoparticles offer a diversity of new technological possibilities for a rapidly growing nanotechnology sector [1], and they can now be found in consumer products (e.g. sun screen, cosmetics, bactericidal agents, medicines, printing ink, computer chips) [2], and in industrial effluents [5-6]. Titanium dioxide (TiO₂) is widely used for their photolytic properties [3]. TiO₂ is a photocatalyst that has been used in solar cells, paints, and coatings, and it is widely used in sunscreens and cosmetics [4].

Public health and environmental impacts: Concern among scientists and regulatory agencies about the potential negative impacts of NPs on human health and the environment is growing as a result of increasing emissions of engineered NPs resulting from their greater application in industrial processes and consumer products. Studies conducted over the past 10 years have provided compelling evidence that a variety of engineered NPs, including metal oxides, fullerenes and carbon nanotubes, can cause toxic effects to mammalian cells [7-9] and other living organisms ranging from bacteria and other aquatic organisms to terrestrial plants [4,10-12]. NPs have been shown to cause disruption of cell membranes, oxidation of proteins, genotoxicity, formation of reactive oxygen species, and release of toxic species [4,13,16]. There is also evidence that NPs can be taken up by cells [13-14] and become systemically distributed throughout the body [13,15].

Environmentall fate of NPs: The concentrations of engineered NPs in natural waters are as yet unknown. Nonetheless, simple box models have predicted concentrations of the most common NPs (Ag and oxides of Ti, Ce, and Zn) in natural waters in the range 1 to 10 µg/L, and total NP concentrations approaching as much as 100 µg/L [36]. In spite of the increasing need to evaluate the effects that NPs may have on the environment, few studies have investigate the transport and fate of nanomaterials in aquatic and terrestrial environments, and little is known regarding interactions of NPs with environmental matrices. NP transport experiments have focused primarily on enhancing delivery of zero-valent iron (ZVI) to soil and groundwater for remediation purposes [32, 37]. Recent studies have also considered the transport of a few other engineered NPs in porous media [38-39].

Fate of NPs in wastewater treatment plants: A significant fraction of engineered NPs can be expected to reach municipal and industrial wastewater treatment plants (WWTPs) since large fractions of these nanomaterials are released to sewer systems [17]. This was recently demonstrated based on a model that considered the environmental fate of various engineered NPs once released from consumer products or industrial processes [18]. Evidence of the occurrence of NPs in municipal WWTPs includes the detection of TiO₂ NPs in the treated effluent from several treatment plants in the USA [19] at concentrations ranging from < 5 to 15 µg/L, and the detection of silver sulfide NPs in sewage sludge from a full-scale municipal WWTP [20]. The release of nano-silver into wastewater from a facility manufacturing nano-Ag containing consumer products (socks with bactericidal silver) has also been observed [21]. The question of whether conventional WWTPs remove NPs has not been examined very thoroughly. Although information on the fate on NPs in WWTP is still very scant, preliminary results [19,22-23] suggest that effluent discharges could represent a significant input of NP into the environment. In locations such as Tucson and other cities in Arizona where aquifer recharge of treated effluents is practiced, NPs carried by the wastewater could potentially be transported to groundwater used for drinking water supply. Therefore, characterization of the fate and behavior of NPs in porous media is needed to quantify exposure scenarios.

A.ii) Objectives

The objective of this research is to determine the extent to which engineered NPs in treated wastewater are attenuated by soil-aquifer treatment. In arid and semiarid environment, aquifer recharge will occur either intentionally (soil-aquifer treatment) or unintentionally (via discharge of effluent to a dry river or discharge via septic drainage fields). One of the aims is to quantify the attenuation of NPs during transport through porous sediment medium. A second aim is to understand the role of organic matter in treated wastewater on the fate of NPs in porous media.

B. Methodology

B.i) Work plan

The proposal included two interrelated tasks as described below:

1. NP characterization. Extensive characterization of the NPs is necessary to interpret fate and transport data. The chemical composition, surface chemistry, specific surface area, crystallinity, particle size and shape, size distribution, agglomeration state, surface charge/zeta potential of TiO₂ NPs will be evaluated as described in the Materials & Methods section.

2. Fate and transport of TiO₂ NPs in porous media: Impact of reclaimed water. The objective of this task is to assess the impact of model wastewater constituents on NP transport. Three contaminants were used to simulate varying contaminants commonly found in aqueous streams. The model organic compounds selected included a non-ionic surfactant, (Triton X-100), an anionic surfactant (ammonium polyacrylate, Dispex A40, BASF, Freeport, TX, USA), a protein (lysozyme, from Sigma-Aldrich) and an aminoacid (glycine from Sigma Aldrich).

B.ii) Materials and methods

Nanomaterials. Nano-sized TiO₂ (21 nm, Aeroxide P25) was obtained from Evonik Industries (Essen, Germany).

Porous media. Quartz sand with an average diameter of 190 μ m was obtained from Acros Organics (Geel, Belgium). The sand was sieved to remove fines and oversized material and then washed several times with acid (HCl, 5%) to eliminate metal oxides coating that could alter its surface chemistry. Subsequently the sand was rinsed with deionized water, and dried for 8 h at 105°C.

Adsorption Isotherms. Batch experiments for determining equilibrium isotherms of the TiO₂ NPs with the three bed materials were conducted in duplicate using a weak phosphate buffer solution (0.5 mM, pH 7, 1.0 mM ionic strength) in glass serum flasks (166 mL) at room temperature (23 \pm 2°C). The solution volume was 50 mL and the initial NP concentration ranged from 5–200 mg/L. From 0.1 to 1.0 g of bed material was added to each flask. NP-free and porous media-free controls were performed concurrently to account for any titanium (Ti) leached from the porous media and for any TiO₂ removal mechanisms not mediated by the media, respectively. Samples were taken of the supernatant both initially and after 3 days of stirring at 150 rpm, which a kinetic study proved to be sufficient time to reach equilibrium. Samples for titanium analysis were taken after allowing the suspensions to rest for 30 min to ensure the settling of the adsorptive media. The amount of TiO₂ adsorbed was determined by mass balance upon correction for any TiO₂ settling observed in the media-free control.

Transport studies - Experiments were performed in similar fashion to previously published methods [52] using a glass column (inner diameter= 15 mm, length= 150 mm, Omnifit Benchmark, Diba Industries, Danbury, CT, USA) packed with sand at room temperature (23 \pm 2°C). Two flow-through quartz cuvettes with 10 mm path lengths (Starna Cells, Inc., Atascadero, CA, USA) were connected to the column influent and effluent using 0.159 cm diameter PTFE tubing. A UV-Vis spectrophotometer (UV 1800, Shimadzu Corporation, Kyoto, Japan) provided absorption data, at 300 nm, monitored by an attached computer at 10 sec intervals. Flow rate control was achieved using a peristaltic pump (Micropuls3, Gilson, Inc., Middleton, WI, USA). Sand columns were dry-packed with 36.5 g of pre-washed sand under agitation from an ultrasonic bath. The column was then filled from the bottom with deionized water at a rate of 2.6 mL/min for 30 min in an ultrasonic bath to ensure wetting of the bed.

A weak phosphate buffer (0.5 mM, pH 7, 1 mM ionic strength) was prepared and any contaminants, when applicable, were added prior to final pH adjustment. Both pH and conductivity measurements were taken for each preparation. A portion of this solution was then separated to pre-rinse the column, displacing 5 bed volumes, so that the conditions on the column were identical to those in the NP suspension. Suspensions of n-TiO₂ (50 mg/L) were prepared in the previously prepared buffer solution by adding the appropriate amount of NPs to 50 mL centrifuge tubes filled with approximately 45 mL of the background solution. These were then sonicated (Ultrasonic Processor, Cole-Parmer, Vernon Hills, IL, USA, 65% intensity, 5 min) and recombined under constant stirring. Both pH and conductivity measurements were again performed to ensure continuity between experimental runs. The NP suspension was pumped through the column at a rate of 2.6 mL/min for 30 bed volumes. Concurrently, samples

were taken at 10 bed volume intervals and tested for size distribution and zeta potential. After 30 bed volumes, the column was rinsed for 5 bed volumes with the background solution. Samples of the column media were then taken at five locations equidistant throughout the column starting at the inlet in order to determine the amount of retained NPs associated with the column media. These experiments were performed in triplicate.

Nanoparticle dispersion stability. The stability of NP dispersions was evaluated by monitoring their particle size distribution (PSD) and zeta potential. Additional information will be obtained by allowing samples to settle for 30-45 min under static conditions, and analyzing samples of the supernatant for PSD, zeta potential, and the concentration of Ti. Samples of the supernatant will be collected carefully to avoid carryover of any settled material.

Analyses. Liquid samples (1 mL) containing TiO₂ were digested in a microwave digester for 30 min at 151°C (25 min ramp time, 1,600 W power) using a mixture of 71% HNO₃ (5 mL) and H₂SO₄ (5 mL) for TiO₂ samples. Soluble Ti was measured by inductively-coupled plasma-optical emission spectrometry (Optima 2100 DV instrument, Perkin-Elmer). NP morphology will be characterized by transmission electron microscopy using a Hitachi S-4800 instrument at 15 kV voltage. The specific surface area of the NPs will be determined using a BET analyzer. The surface chemistry and crystallinity of the NPs will be characterized using X-ray photoelectron spectroscopy (Kratos 165 Ultra XPS) and XR diffractometer (Scintag XDS 2000 PTS), respectively. NP solubility will be determined by filtration through a 1-nm cutoff membrane.

The zeta potential of NPs in aqueous solution will be measured with a Zeta Sizer Nano ZS instrument (Malvern, Inc.) using the Smoluchowski equation to correlate particle electrophoretic mobility to zeta potential. Particle size distribution measurements will be determined by dynamic light scattering using the same instrument. Wastewater analysis (pH, chemical oxygen demand, BOD, suspended solids, alkalinity, etc.) will be performed according to standard methods [35].

NPs were imaged by transmission electron microscope using a Hitachi H8100 at 200 keV. Surface area measurements were obtained by nitrogen gas adsorption using a Beckman Coulter SA 3100 (Beckman Coulter, Inc., Brea, CA) and the pore distribution data was deduced using a cylindrical pore model.

C. Principal findings and significance

C.i) NP characterization

Transmission electron microscopy imaging of the n-TiO₂ displayed crystalline and nearly spherical particles (Fig 1). The TiO₂ NPs (dry powder) had a reported primary particle size of 21 nm. The average particle size of n-TiO₂ in aqueous solution at pH 7 was significantly higher (200±2 nm) suggesting some aggregation (Fig. 2). At the same pH value, the zeta potential of n-TiO₂ was very low (-41.7±3.7 mV), which is indicative of a stable colloidal dispersion. The results of potentiometric titration (Fig. 3) indicated that the isoelectric point of n-TiO₂ was 4.1.

XR diffraction analysis showed that the material consisted chiefly of anatase and rutile. A recent study found that composition ranged from 73-85 % anatase, 14-17 % rutile and 0-18 % amorphous TiO₂ [40].

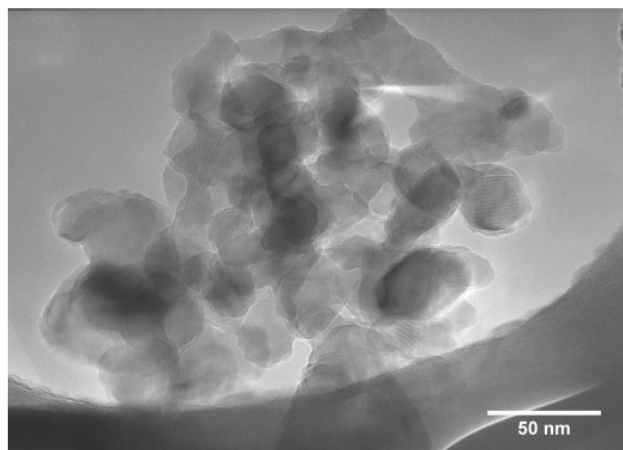


Figure 1. Transmission electron microscopy image of the n-TiO₂.

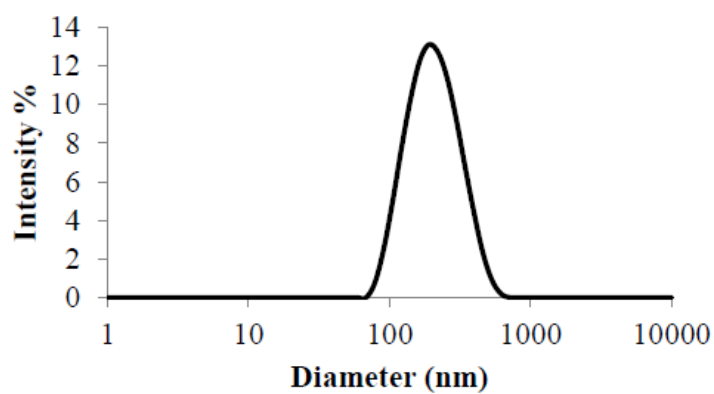


Figure 2. Particle size distribution of the nano-TiO₂.

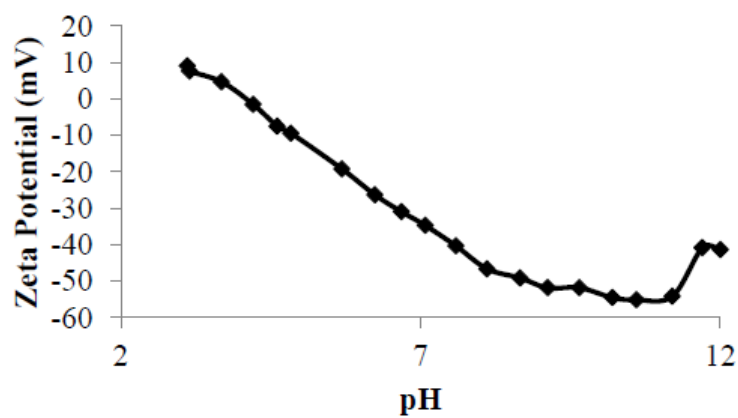


Figure 3. Zeta potential of n-TiO₂ as a function of pH.

C.ii) Sand characterization

The physical structure and surface properties of granular media is a major factor determining the retention of colloidal material during porous media filtration. A more porous material may allow for additional surface area or more dead volume for the NPs to become trapped in. Also, a rougher material provides a more tortuous path for the NPs which increases physical entrapment. Scanning electron microscopy analysis confirmed that the sand used had a smooth surface and was non-porous. In agreement with these observations, the surface area of the sand (BET technique) was very low ($< 0.05 \text{ m}^2/\text{g}$). Surface charge measurements at different pH values revealed that the apparent surface charge of sand is negative across circum-neutral and high pH ranges. The surface charge at pH 7 is of particular interest as that is the operating pH of the column experiments. At that pH value, sand has a highly negative surface charge (-21.68 C m^{-2}). The isoelectric point determined for the sand was 3.45.

C.ii) Fate and transport of TiO_2 NPs in porous media: Impact of reclaimed water

Three contaminants were used to simulate varying contaminants commonly found in aqueous streams. An ammonium polyacrylate surfactant (Dispex A40) was selected as a model surfactant and dispersant. Lysozyme and glycine are two model organic compounds with disparate points of zero charge (pH_{pzc}), 9.60 and 5.97, respectively [41-42]. The choice of organic compounds with respective pH_{pzc} values above and below the tested pH of 7.0 provided information that can be used to predict the interaction of positively and negatively charged organic molecules with n- TiO_2 .

Table 1 lists the average particle size and zeta potential of n- TiO_2 before and after addition of the three model contaminants. When no contaminant was added, the n- TiO_2 showed a consistent average particle size of 200 nm. While NP dispersions amended with Dispex and glycine displayed little departure from the virgin material, lysozyme showed significant potential for inducing n- TiO_2 aggregation (Fig. 4). The NP dispersion amended with lysozyme rapidly aggregated to approximately 350 nm and then slowly trended toward 500 nm. The rapid aggregation observed in assays with lysozyme is consistent with the zeta potential shift induced by the protein.

Table 1. Zeta potential of TiO_2 nanoparticles in the presence and absence of organic additives at pH 7.0.

Solution	Zeta Potential (mV)
<i>No Contaminant</i>	-41.7 ± 3.7
<i>Dispex</i>	-50.5 ± 2.5
<i>Lysozyme</i>	17.6 ± 2.3
<i>Glycine</i>	-43.2 ± 2.8

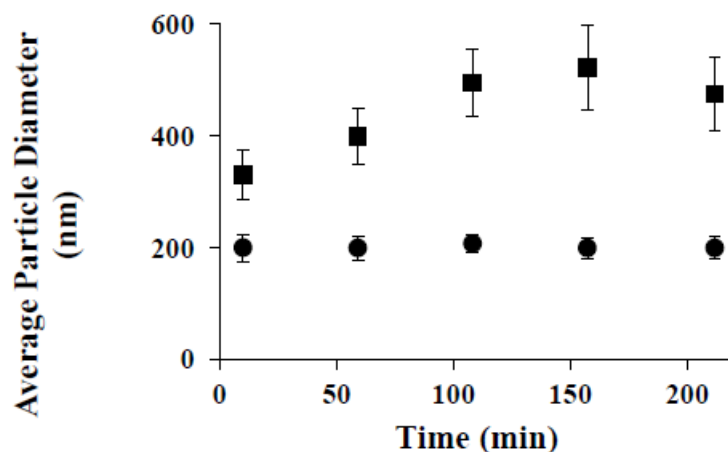


Figure 4. Average hydrodynamic diameter of n-TiO₂ aggregates as a function of time for the cases of no contaminant (●) and lysozyme (■).

While the zeta potential was -41.7 mV in assays lacking contaminant, there was a positive shift when lysozyme was added (17.6 mV). This shift is due to the net positive charge of the NP surface which results from sorption of lysozyme which is positively charged at pH 7 (high pH_{pzc} of 9.60). It is generally held that NP suspensions with a zeta potential less than 20 mV in magnitude will readily aggregate. The polyacrylate dispersant caused only a small reduction in the average size of TiO₂, 195 nm, which corresponds to the further reduction in zeta potential, -50 mV. Glycine addition only caused a slight decrease in zeta potential (-43.2 mV). This decrease corresponds with the expected negative charge of glycine (pH_{pzc} = 5.97) at pH 7.

C.iii) Adsorption Isotherms

There are four major mechanisms for NP capture in porous media: sedimentation, interception, straining, and diffusion or selective adsorption [44]. The first three are physical interactions determined to a large extent by the structure and packing of the porous material, while diffusion or selective adsorption is controlled by surface interactions. In order to separate physical interactions from surface adsorption, batch isotherms were performed with n-TiO₂ and sand (Fig. 5). Sand displayed very low affinity for n-TiO₂ at pH 7. For example, at an equilibrium concentration of approximately 50 mg TiO₂/L, the n-TiO₂ loading determined for sand was only 0.02 mg TiO₂/g medium. The low adsorption capacity observed was expected given the negative surface charge of sand and n-TiO₂ under circum-neutral pH conditions.

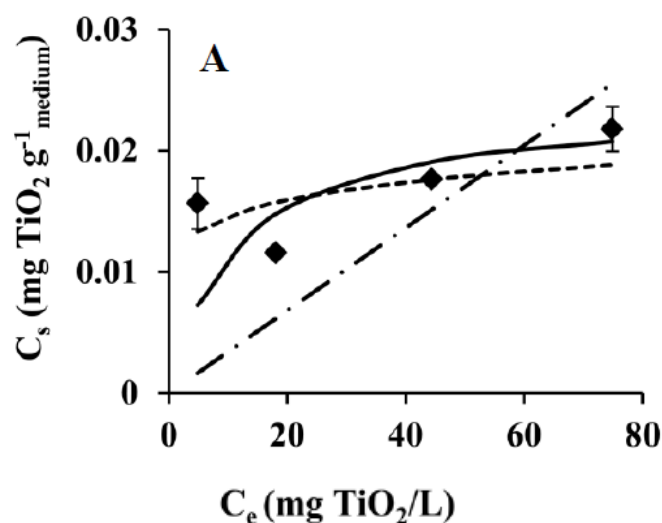


Figure 5. Association isotherms for n-TiO₂ onto sand. Henry (— · —), Freundlich (---), and Langmuir (—) isotherm fits.

C.iv) Fate and Transport of TiO₂ NPs during Porous Media Filtration

Figure 6 compares the relative effluent NP concentration with respect to time determined for n-TiO₂ dispersions in flow-through column experiments packed with sand. Plots of the NP concentrations associated with the filtration medium as a function of relative bed depth are shown in Figure 7. Sand was highly ineffective as an absorbent material, with breakthrough being reached in less than two bed volumes (Fig. 6). Sand had a very small surface area and very little surface roughness, so physical interactions are unlikely to play a major role in retention under these conditions. This curve does match well with DLVO predictions, with the repulsive electrostatic interaction between the negatively charged n-TiO₂ and the negatively charged sand surface greatly outweighing the attractive van der Waals interactions.

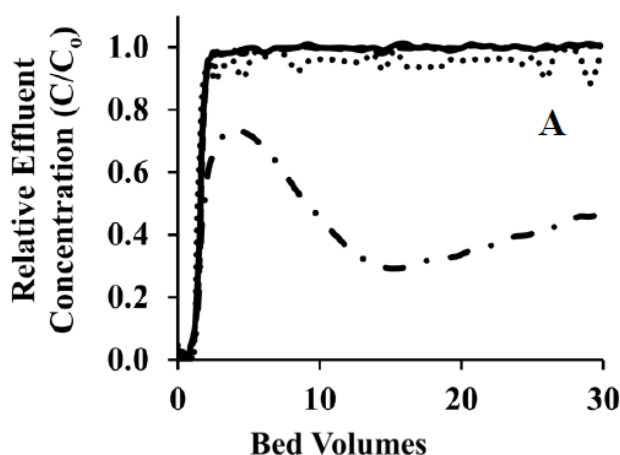


Figure 6. Relative effluent n-TiO₂ concentration as a function of the number of bed volumes processed for sand. Plots for dispersions with no contaminant (—), and for dispersions amended with Dispex (---), lysozyme (— · —), and glycine (···).

The captured NP concentration is extremely low; around 0.01 mg TiO₂/g sand for the entire bed length (Fig. 7). Overall, the physical characteristics of sand do not aid in the retention of the n-TiO₂ and the repulsive electrostatic interactions dominate resulting in essentially zero retention [45-47].

C.v) Effect of solution contaminants on n-TiO₂ fate and transport during porous media filtration

The presence of organic contaminants impacted the transport and retention of n-TiO₂ in saturated sand columns. The model dispersant, Dispex, proved to be very effective in reducing n-TiO₂ retention during bed filtration. Although no departure from the baseline lacking Dispex can be observed for the sand bed (Fig. 6) due to the overall poor retention of sand, the impact of Dispex on NP retention was clearly observed in the columns packed with activated carbon (results not shown), with immediate full breakthrough for n-TiO₂ dispersions amended with the dispersant. Other dispersants have been shown to decrease NP retention [48-49] and studies have concluded this to be due to steric hindrances due to the adsorbed species [47,50]. Figure 7 shows the profiles of n-TiO₂ retained in the sand bed. This data supports the effluent concentration curves as the dispersant-contaminated n-TiO₂ is consistently the least retained in all bed materials.

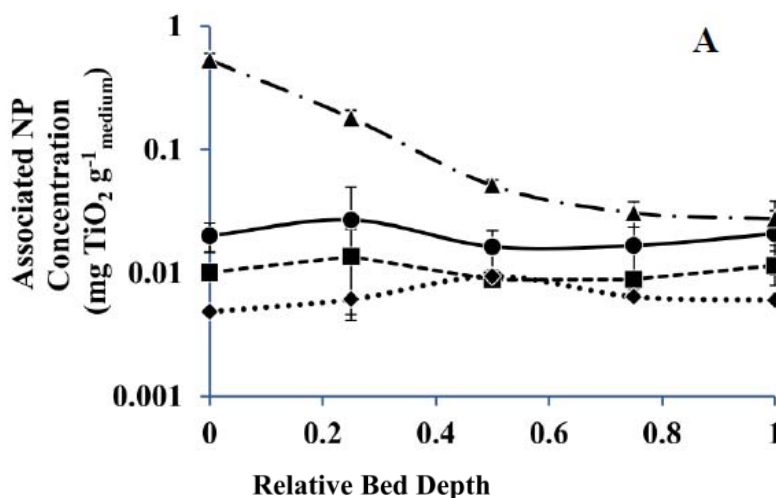


Figure 7. TiO₂ nanoparticle concentrations associated with porous media as a function of bed depth for sand. Four cases shown: no contaminant (—●—), Dispex (—■—), lysozyme (—▲—) and glycine (···◆···).

Addition of glycine did not lead to significant departure from the baseline case without contaminants in size or zeta potential, nor did it change the retention behavior in sand beds. In contrast, lysozyme greatly influenced n-TiO₂ retention. Results for lysozyme addition to the NP dispersion with sand as the filtration medium provide an excellent model case for filter ripening (Fig. 6). Here, as the lysozyme-coated NPs associate with the sand surface, the NPs themselves, destabilized by the addition of lysozyme onto their surface, become more efficient collectors than the bare sand surface, providing the characteristic “hump” in the breakthrough curve. While destabilization due to lysozyme addition did add to NP retention, a significant fraction of the n-TiO₂ eluted from the column. The retained n-TiO₂ bed profile for lysozyme contamination on the sand bed displayed a linear decrease over the bed length (Fig. 7), which exposes an

exponential decay characteristic of strong interactions between adsorbent and adsorbate. This could be either due to capture approaching capacity before moving down the column in the classical “front” or due to physical straining occurring near the inlet of the column. Due to the highly aggregated state of the lysozyme coated n-TiO₂ (> 500 nm); physical straining is the more likely cause.

The combined results of the contaminants and the variability in their effects displays the importance of a comprehensive investigation of any targeted wastewater stream to determine the competing roles the varying contaminants contained will play.

C.vi) Environmental Implications

A recent study has predicted that almost 3,000 tons of n-TiO₂ are released yearly from production, manufacturing and consumption in the United States alone [51]. This, combined with the increasing public concern about the safety of nanomaterials indicates the importance of understanding the environmental fate of n-TiO₂ and other nanomaterials. Improved knowledge of the behavior of engineered nanomaterials in porous media is particularly important since aquifer recharge with treated wastewater has the potential to introduce NPs into groundwater resources.

The results of n-TiO₂ transport experiments in saturated sand media confirmed that organic contaminants can have a strong impact on the transport and retention of nanoparticles. In the absence of organic contaminants, n-TiO₂ was poorly retained by the sand bed. The mobility of n-TiO₂ was altered to various degrees when model organic compounds were present in solution. This is due to the impact of organic additives on the stability of nanoparticle dispersions as well as the interaction between NP-granular media. In addition to organic contaminants, the presence of inorganic ionic species in treated wastewater is known to impact the state of aggregation and mobility of nanoparticles in saturated porous media [24]. In conclusion, these results indicate that the ultimate fate of nanomaterials during aquifer discharge will strongly depend on the composition of the treated wastewater. The nature of the nanomaterial considered and properties of the subsurface media should also be expected to impact nanoparticle-geomedia interactions and, thus, the ultimate fate of engineered nanomaterials during aquifer recharge with treated wastewater.

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"Does Increasing Solids Retention Time in the Wastewater Treatment Process Affect the Persistence of Antibiotic Resistance Genes?"

Basic Information

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"Does Increasing Solids Retention Time in the Wastewater Treatment Process Affect the Persistence of Antibiotic Resistance Genes?"

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Problem and Research Objectives:

A 2000 World Health Organization report focused on antibiotic resistance (AR) as one of the most critical human health challenges of the next century and heralded the need for “a global strategy to contain resistance” [1]. According to the report, more than 2 million Americans are infected each year with resistant pathogens, and 14,000 die as a result. Following their use, it is estimated that up to 75% of antibiotics are excreted unaltered or as metabolites [2]. Unfortunately, most wastewater treatment plants (WWTPs) are not designed for the removal of these micro-pollutants, and as a result, residual antibiotics are released into the environment with treated wastewater, leading to concern regarding their contribution to AR in environmental microorganisms [3]. There also exists the potential for wastewater treatment (WWT) processes to select for the survival of resistant microorganisms. Thus, it has been proposed that resistance development during WWT is an important and key source of AR in the environment [4]. And yet, few studies have attempted to identify processes contributing to the selection of AR bacteria. Such information will be critical in the development of WWT strategies to reduce environmental transfer of AR bacteria.

During the conventional activated sludge (CAS) step of WWT, the wastewater containing organic matter is aerated in a basin in which micro-organisms metabolize the suspended and soluble organic matter. Because CAS, by its very design, exposes bacteria to ideal growth conditions and relatively high concentrations of antibiotics, it is hypothesized that CAS may increase AR development. Direct correlations between solids retention time (SRT) and reductions in antibiotics have been shown [5, 6], but higher SRTs also provide prolonged exposure of bacteria to influent antibiotic levels. This study proposed to assess the effects of varying SRT in full-scale activated sludge processes on the degradation of trace antibiotics and microbial selection for AR. As the adoption of recycled water (including Indirect Potable Reuse) becomes more widespread, and as the public comes into contact with recycled water at a higher frequency, there will be increased pressure for utilities and other water managers to better understand the microbial population dynamics. Of critical importance will be an improved understanding of microbial populations that could pose a risk to the public. Standardized qualitative and quantitative methods must be developed to better understand risk. A detailed assessment of rates in AR development and identification of bacterial processes contributing to AR will aid in technological advances to decrease the prevalence of AR in recycled water, alleviating environmental and public health concerns.

This study included a comprehensive evaluation of temporal variability in loadings of antibiotic concentrations in the WWT process, quantification of genes conferring AR to bacteria, and examination of relative proportions of AR *E. coli* (Gram negative) and *Enterococcus* (Gram positive) in raw wastewater, activated sludge solids, and finished effluent from a range of

treatment facilities. The primary goal of this research was to focus on operational conditions during biological treatment, since these processes may pose the greatest risk for the development of AR populations. By monitoring several locations within the WWT train, project team was able to characterize the impact of WWT on AR prevalence and, in turn, to depict the downstream impacts of recycled water on end-users and the environment. Ultimately, this study will provide utilities with new knowledge and tools for treatment process optimization and AR mitigation.

Methodology:

Task 1: Literature Review. The first task involved a review of available literature related to AR in water supplies, supplemented with a review of occurrence and usage patterns for widely used prescription pharmaceuticals, including human metabolism rates, and susceptibility to common WWT processes. Five target antibiotics (sulfamethoxazole, trimethoprim, ampicillin, tetracycline, vancomycin) and their associated quantitative analytical methods (described below) were finalized during this task. This task concluded with the selection of the quantitative PCR (qPCR) assays for enumeration of select bacterial genes conferring resistance to the target antibiotics (Table 1).

Table 1. qPCR Assays for Antibiotic Resistance Gene Analysis

Primers	Assay Target	Sequences	Amplicon size (bp)	References
<i>sulI</i> -F <i>sulI</i> -R	Sulfamethoxazole	cgcaccggaaacatcgctgcac tgaagtccgccgaaggctcg	163	Pei et al., 2006
<i>sulII</i> -F <i>sulII</i> -R	Sulfamethoxazole	tccggtggaggccggtatctgg cgggaatgccatctgcctgag	191	Pei et al., 2006
<i>dfr1</i> -F <i>dfr1</i> -R	Trimethoprim	cgaagaatggagttatcggg tgctggggatttcaggaaag	372	Grape, M., 2007
Lak2-F Lak1-R	Ampicillin	gggaatgctggatgcacaa catgaccagttcgccatc	189	Volkman et al., 2003
<i>tetW</i> -F <i>tetW</i> -R	Tetracycline	gagagcctgctatatgccagc ggcgctatccacaatgtaac	168	Aminov et al., 2001
<i>vana3</i> -F <i>vana3</i> -R	Vancomycin	ctgtgaggtcggtgtgctg tttggtccacctcgcca	377	Volkman et al., 2003; Merlino et al., 2010
GFD-F GFD-R	<i>Helicobacter</i> spp.	ctatgacgggtatccggc attccacctacctcctcca	376	Proietti et al., 2010; Green et al., 2011
Bac-F Bac-R	Bacteria 16s rRNA	atggtgtcgtcagct acgggcgggtgtgtac	370	Ritalahti et al., 2006

Task 2: Full-Scale Sampling to Quantify Antibiotic and AR Loadings. During previous research projects (WERF-CEC4R08, WRF-08-05, and WRF-09-10), the project team developed collaborative relationships with WWTPs throughout Arizona and the U.S. These existing collaborations provided a foundation for this study, and eight facilities were selected based on their range in operational conditions specifically related to SRT (1.5 to 25 days). Samples were

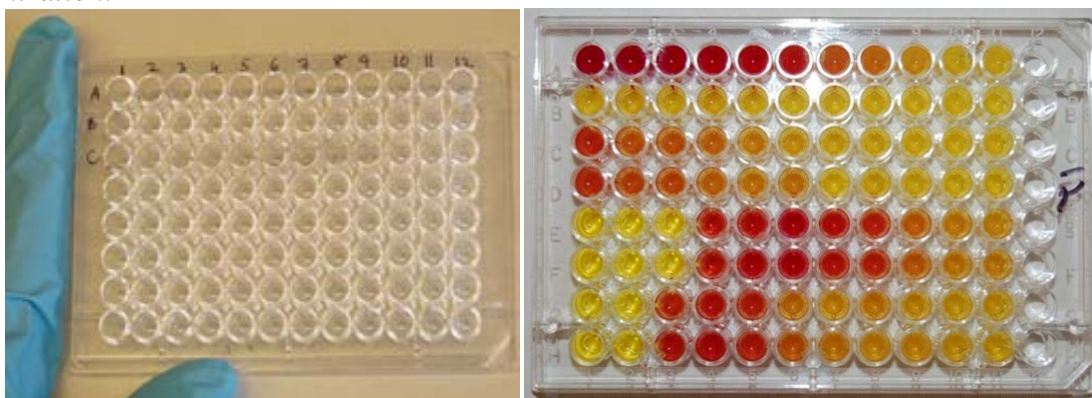
collected at two locations within each WWTP. For the microbial analyses described below, samples were collected from the primary clarifier and the discharge from the activated sludge basin (immediately prior to the secondary clarifiers). The suite of antibiotics finalized in Task 1 was quantified in the primary and secondary effluent.

Task 3: Analysis of Full-Scale Sampling Data. During Task 1, the treatment trains included in this study were characterized based on unit processes and operational conditions. Although the entire treatment train was characterized, we focused on conditions associated with CAS since this process may provide the greatest potential for the development of AR. The conditions encompassed by the selected facilities allowed the project team to identify the operational parameter(s) with greatest impact on AR prevalence. This was accomplished by evaluating correlations between each operational variable (e.g., SRT, type of biological treatment) and the relative concentrations of AR microbes and genes.

Antibiotic concentrations were analyzed using automated solid phase extraction (Dionex), isotope dilution, liquid chromatography (Aquity UPLC, Waters), and tandem mass spectrometry (MS/MS; Quattro Premier XE, Waters) in the Arizona Laboratory for Emerging Contaminants (ALEC) at the University of Arizona. Studies have shown that trace concentrations of antibiotic compounds in treated effluent are significantly lower than the antibiotic concentrations commonly used for resistance evaluation. For the microbial samples, *E. coli* and *Enterococcus* were selectively enriched and isolated on agar plates.

Individual *E. coli* and *Enterococcus* isolates were added to 96-well plates serially diluted with target antibiotics (Fig. 1). Following a 24-h incubation period, sample absorbance at 600 nm, which is indicative of microbial growth, was quantified for each well. According to CLSI standards [10], the minimum inhibitory concentration (MIC), or the lowest antibiotic concentration that inhibits visible growth, was reported for each isolate. According to our hypothesis, isolates collected from facilities with higher SRTs should be characterized by higher MICs.

Figure 1. The image below shows a 96-well plate experimental set up. A single isolate in growth medium was added to all cells in columns A and B, while column C received medium only as negative growth control. Rows 2-8 were pre-loaded with antibiotics. Row 1 = positive growth control wells; no antibiotic. Row 2 = lowest level of antibiotic; Row 3 = 2X antibiotic concentration of Row 2; Row 4 = 2X antibiotic concentration of Row 3...Row 8 = highest concentration.



Finally, DNA was extracted in triplicate from each raw sample collected through the WWT train. Real-time qPCR was used to quantify genes within the DNA encoding resistance to target antibiotics. Internal control DNA from *Helicobacter* spp. (GFD; Table 1) was spiked into each sample prior to DNA extraction to quantify DNA extraction efficiency. Finally, conserved portions of the Universal 16Sr RNA gene were quantified within each sample (Table 1) to standardize PCR results and allow for direct comparison between samples. Our hypothesis for this Task was that AR genes would be expressed with higher frequency in samples collected from facilities with higher SRTs.

Principal Findings and Significance:

Results from this study suggest that while prolonged SRTs may be beneficial at reducing residual levels of trace organic contaminants they also may prolong the exposure of native microbial populations to antibiotics and thus confer antibiotic resistance. In this study we evaluated eight wastewater treatment facilities with SRTs ranging from 1 to 25 days (Table 2.)

It is anticipated that results of this work could permit optimization of SRT at each facility for the enhanced degradation of Trace Organic Contaminants as well as reduction in Antibiotic Resistant microorganisms.

Table 2. Wastewater Treatment Plant Operational Parameters. Treatments included; Trickling Filter (TF); Conventional Activated Sludge (CAS); Chlorination (Cl); Ultraviolet Light (UV); Membrane Bioreactor (MBR); and Sequencing Batch Reactor (SBR).

WWTP Site	SRT (days)	BOD (mg/L)	MGD	Treatment
Plant 1	1-2	243	35	TF
Plant 2	2-4	253	9	CAS/Cl/UV
Plant 3	4	263	8	MBR
Plant 4	8-9	167	9	CAS/Cl/UV
Plant 5	14	210	2	CAS/Cl/UV
Plant 6	17	245	10	CAS/Cl/UV
Plant 7	19	328	135	CAS/Cl/UV
Plant 8	25	282	2	SBR

The following tables (Tables 4 – 8) represent the percentage of bacterial isolates classified as “resistant” as defined by the Clinical and Laboratory Standards Institute (CLSI). CLSI updates and standardizes MIC levels at which bacteria are considered “resistant” (Table 3). Individual

isolates were screened against a range in concentrations of antibiotics that bracketed the CLSI standards.

Table 3. Clinical and Laboratory Standards Institute (CLSI) Standards for Target Resistance

Antibiotic	Concentration Range Tested (µg/ml)	Target Resistance (µg/ml)
Tetracycline	2-128	≥16
Sulfamethoxazole	8-512	≥64
Trimethoprim	2-128	≥16
Ampicillin	2-128	≥32
Vancomycin	0.5-32	≥4

Table 4. Vancomycin % Isolates Tested that Displayed High Level Resistance

Vancomycin	Primary Treatment	Secondary Treatment
SRT of 3 days	95%	63%
SRT of 9 days	95%	90%
SRT of 19 days	95%	83%

Table 5. Sulfamethoxazole % Isolates Tested that Displayed High Level Resistance

Sulfamethoxazole	Primary Treatment	Secondary Treatment
SRT of 3 days	29%	0%
SRT of 9 days	37%	37%
SRT of 19 days	8%	29%

Table 6. Ampicillin % Isolates Tested that Displayed High Level Resistance

Ampicillin	Primary Treatment	Secondary Treatment
SRT of 3 days	58%	0%
SRT of 9 days	45%	37%
SRT of 19 days	95%	75%

Table 7. Trimethoprim % Isolates Tested that Displayed High Level Resistance

Trimethoprim	Primary Treatment	Secondary Treatment
SRT of 3 days	75%	33%
SRT of 9 days	45%	20%
SRT of 19 days	75%	75%

Table 7. Tetracycline % Isolates Tested that Displayed High Level Resistance

Tetracycline	Primary Treatment	Secondary Treatment
SRT of 3 days	95%	45%
SRT of 9 days	75%	45%
SRT of 19 days	95%	75%

For each of the five antibiotics evaluated across the range of SRTs, a general trend of decreasing percent resistance in effluent collected from the primary treatment to samples collected from the secondary clarifier. This indicates that the treatment process at each of the facilities is effective at reducing some level of resistance in the bacterial populations. However, when evaluating the total percent resistance after secondary treatment, facilities with SRTs of 3 days ranged from 0% to 63% resistance while SRTs of 19 days had substantially higher levels of resistance ranging from 29% to 83%. This result supports the hypothesis that increasing SRT aids the persistence and development of antibiotic resistant bacterial populations.

An additional way of interpreting the development of antibiotic resistance is to measure the Minimum Inhibitory Concentration (50) or MIC₅₀. While high level resistance (Tables 4-8) indicates results based on single isolates, MIC₅₀ represents resistance in a large group or organisms. MIC₅₀ is defined as the antibiotic concentration required to inhibit the growth of 50% of organisms within a bacterial population. Tables 9-13 represent the MIC₅₀ for low (3 days), midrange (9 days), and high (19 days) SRTs for each of the 5 antibiotics evaluated.

Table 9. Vancomycin MIC₅₀

Vancomycin	Primary Treatment	Secondary Treatment
SRT of 3 days	32 µg/ml	16 µg/ml
SRT of 9 days	8 µg/ml	32 µg/ml
SRT of 19 days	8 µg/ml	32 µg/ml

Table 10. Sulfamethoxazole MIC₅₀

Sulfamethoxazole	Primary Treatment	Secondary Treatment
SRT of 3 days	32 µg/ml	8 µg/ml
SRT of 9 days	16 µg/ml	32 µg/ml
SRT of 19 days	16 µg/ml	32 µg/ml

Table 11. Ampicillin MIC₅₀

Ampicillin	Primary Treatment	Secondary Treatment
SRT of 3 days	64 µg/ml	32 µg/ml
SRT of 9 days	64 µg/ml	64 µg/ml
SRT of 19 days	64 µg/ml	128 µg/ml

Table 12. Trimethoprim MIC₅₀

Trimethoprim	Primary Treatment	Secondary Treatment
SRT of 3 days	32 µg/ml	8 µg/ml
SRT of 9 days	64 µg/ml	32 µg/ml
SRT of 19 days	64 µg/ml	32 µg/ml

Table 13. Tetracycline MIC₅₀

Tetracycline	Primary Treatment	Secondary Treatment
SRT of 3 days	128 µg/ml	64 µg/ml
SRT of 9 days	32 µg/ml	32 µg/ml
SRT of 19 days	64 µg/ml	128 µg/ml

Results from the MIC₅₀ analysis agree with results from the percent resistance analysis in that SRTs of 3 days show a decrease in the concentration of antibiotic needed to inhibit 50 percent of the bacterial population from the primary clarifiers to secondary treatment. This result was seen for all five antibiotics evaluated. Additionally, four out of the 5 antibiotics evaluated revealed, increases in the MIC₅₀ for SRTs of 19 days suggesting that increasing SRT induces resistance to each individual antibiotic and thus a higher concentration of antibiotic is required to inhibit growth of 50% of the bacterial isolates evaluated.

Summary of Conclusions:

- Results indicate the presence of all target resistance genes (Table 1) from the five antibiotics evaluated along the treatment train of each facility tested.
- Quantitative data indicate that antibiotic resistance genes are decreasing along the treatment train; however, target genes are still found at detectable levels towards the end of treatment.
- Normalized numbers of copies of Bacterial 16S rRNA genes were similar through treatment indicating that while bacteria community composition may change during treatment, total bacterial population concentrations remain essentially unchanged through the treatment process.
- All wastewater treatment plants evaluated were effective at lowering the percentage of resistant bacterial isolates from primary to secondary treatment indicating the success of the treatment regimes in Arizona.
- Solid Retention Times ranging from 1 to 6 days appeared to be the most effective at mitigating antibiotic resistance when compared to SRTs of 9 to 25 days.
- Approximately 35% of isolates showed multiple drug resistance (MDR) indicating resistance to at least 2 antibiotic compounds evaluated.
- Multiple variables within wastewater treatment outside of CAS should be investigated further to better understand the true impact of wastewater treatment on trace organics and their impact on microbial populations. Including: heavy metals, anoxic zones, the denitrification processes, disinfection processes, etc.
- Future investigation should include tertiary treatment and evaluate the presence of antibiotic resistant bacterial isolates and resistance genes in the final effluent. In addition, future work must evaluate the impact of resistance bacteria and genes on development of

biofilms within water transport systems and on native bacterial populations in the environment.

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Toxicity of Emerging Contaminants in an Effluent Dependent Stream: the Role of Suspended Solids and Sediments

Basic Information

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Principal Investigators:	David Matson Quanrud, Robert Arnold, Eduardo Saez, Shane Snyder

Publications

There are no publications.

a. PROBLEM AND RESEARCH OBJECTIVES

Many substances used in domestic households are persistent and pass through conventional wastewater treatment. Among these, chemicals of emerging concern (CECs), including endocrine disrupting compounds (EDCs), are of particular interest. In a 2002 nationwide survey, the USGS measured some of the highest in-stream concentrations of EDCs in the effluent-dependent lower Santa Cruz River (SCR) near Tucson. Targeted testing by the City of Tucson during 2009 and 2010 under their Microconstituent Sentinel Program detected the compounds perfluorooctane sulfonate (PFOS), carbamazepine, and sulfamethoxazole in three groundwater production wells located along the lower SCR (15-20 mi downstream from wastewater effluent outfalls), suggesting that extracted ground water may include a component of effluent origin. Clearly, concern is warranted regarding the presence and fate of CECs in the Lower SCR watershed.

To better understand CEC loadings to the effluent-dependent lower SCR in Tucson, a 2011 investigation by PIs Quanrud and Snyder investigated the presence and fate of a suite of 13 representative CECs during river transport along a 22-mile reach of the lower SCR. A series of groundwater monitor wells located along that same reach was also sampled to assess CECs fate following riverbed infiltration/percolation of effluent. While that study provided substantial new information on transport and fate of selected emerging organic contaminants in the Lower SCR Watershed, it was limited to examining only liquid-phase CECs concentrations and did not assess toxicity or endocrine disruption activity. Many CECs have moderate to high hydrophobicity (high log K_{ow} values) and tend to partition to the solid-phase. Suspended solids in effluent discharged to the SCR are thus a potentially significant additional source of hydrophobic CECs to the Santa Cruz watershed that were not accounted for in previous investigations. CECs may accumulate in riverbed sediments due to deposition of suspended solids as well as by sorption during effluent infiltration/percolation in the riverbed.

The ecological impact of current CECs loading to sediment in the SCR is unknown but it is reasonable to postulate that benthic organisms uptake CECs and that at least some compounds are biomagnified up the food chain. With the expectation of improved river water quality after completion of SCR wastewater treatment plant upgrades in 2015, reestablishment of fish populations, as has already occurred downstream of the newly upgraded Nogales International Wastewater Treatment Plant located on the Upper SCR, may in fact facilitate a greater biomagnification of some CECs to newly re-established aquatic organism populations and higher-level predators (e.g. fish-eating birds and/or mammals).

Here, we assessed endocrine disruption activities in liquid-phase wastewater effluent, suspended solids, and riverbed sediments as a function of downstream travel distance. A combination of bioassays was used to assess estrogenic and androgenic activities: the Yeast Estrogen Screen (YES) and Yeast Androgen Screen (YAS) reporter gene assays. The present study was motivated by the need to assess the transport and fate of CEC toxicity contribution provided by the solid-phase in an effluent dependent stream, along with the need to establish baseline data in the Santa Cruz River prior to the 2015 completion of upgraded treatment processes at the two Pima County municipal wastewater treatment facilities that will substantially improve effluent quality and river health.

b. METHODOLOGY

General. A three-pronged sampling approach was performed that included collection of liquid phase, suspended solids, and riverbed sediments at six locations along a 37-km reach of the Lower SCR (Figure 1). Liquid samples (3L) were collected using pre-cleaned and muffled amber glass bottles and filtered within 24 hours of collection using 0.7 μm glass fiber filter membranes (Whatman). Filter membranes were extracted as described below to recover CECs associated with the suspended solids fraction of the samples.

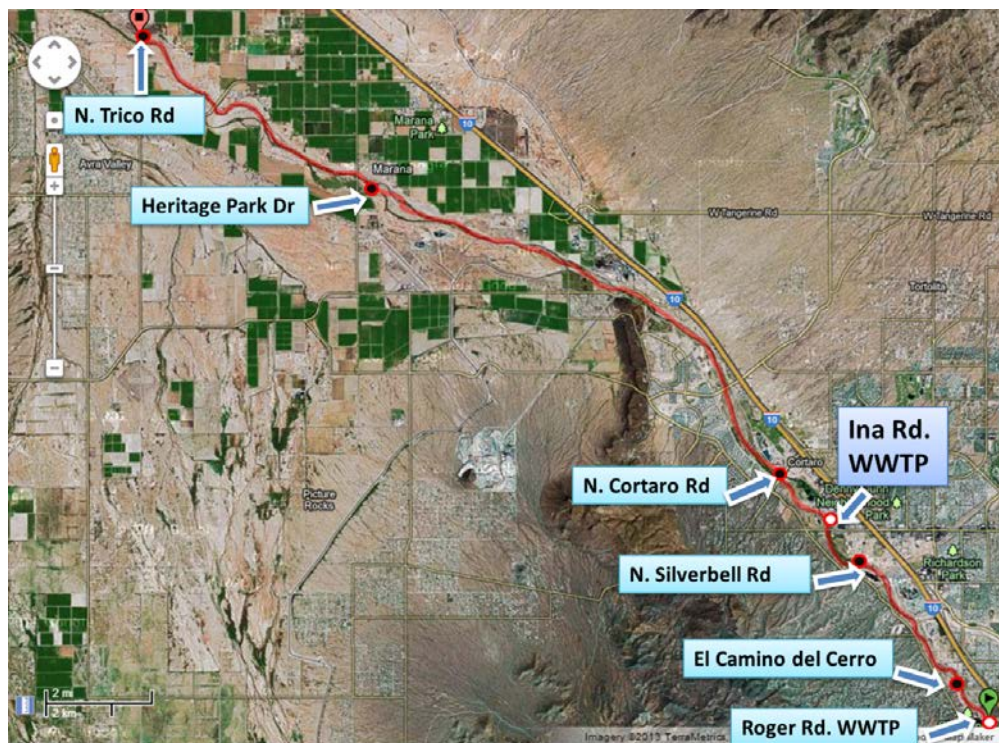


Figure 1. Aerial map showing the six sampling locations along the 37-km reach of the lower Santa Cruz River extending northwest from the City of Tucson, Arizona.

Riverbed sediments were collected proximate to the Roger Road effluent outfall and at five additional locations downstream to Trico Road (Figure 1, Table 1). At each location, riverbed sediments were collected at two depths: 0-3 cm and 10-12 cm using pre-cleaned and muffled amber glass jars. Each sediment sample was a composite composed of at least 2 replicates obtained along a cross section of the river at each location. Sediment sampling was performed before (6-22-13) and after (7-18-13 and 10-13-13) the summer monsoon storm season in order to assess impacts of scouring/deposition on sediment-bound estrogenic activity. Since flow rates in the Santa Cruz can increase substantially during summer stormwater runoff events, which are known to scour and transport riverbed sediments, sediment sampling was performed before and after the summer rainstorm season to assess associated impacts on sediment-bound endocrine disruption activities.

Table 1. Sampling locations for liquid phase, suspended solids, and riverbed sediments along the 37-km reach of the lower Santa Cruz River near Tucson, Arizona.

Sampling Site Name	Distance downstream, km (mi)	Location
Roger Rd outfall	0.00 (0.00)	32°17'4"N, 111°1'46"W
El Camino del Cerro Rd	1.49 (0.93)	32°17'42"N, 111°2'18"W
N Silverbell Rd.	7.18 (4.49)	32°19'41"N, 111°4'26"W
N. Cortaro Rd.	10.91 (6.82)	32°21'8"N, 111°5'46"W
Heritage Park Dr.	26.75 (16.72)	32°25'31"N, 111°12'57"W
N. Trico Rd.	37.25 (23.28)	32°28'17"N, 111°18'14"W

Sample Preparation/Extraction. All analytical work was performed in laboratories located in the Department of Chemical and Environmental Engineering on the University of Arizona campus. Aqueous-phase samples sometimes require a degree of “cleaning” and analyte concentration, which can be carried out by solid phase extraction (SPE) and elution from the SPE resin in a stepwise methanol gradient. Compounds more hydrophobic than *p*-nonylphenol ($\log K_{OW} \sim 4.5$) tend to be retained on reverse phase resins, even through alcohol elution steps, and can be separated from the estrogens and estrogen mimics in this way. The technique is equally useful for androgen separations. Concentration factors >103 are conveniently obtained by processing initially large water volumes—on the order of a few liters. The *in vitro* endocrine disruption activity tests require an aqueous-phase sample, so that the methanol/water eluent must be evaporated before analytes are redissolved in water. Solid-phase samples like dried sludge or sediment/soil provide a more formidable challenge. Analytes were separated from bulk solids in an adaptation of microwave accelerated extraction (MAE). The MAE procedure developed here is relatively gentle, involving low heats/pressures during 30-min extractions in methanol. Extracts were diluted in ultrapure water, and the methanol water mixtures then processed using normal SPE procedures (above).

Endocrine Activity Assays. In both the yeast estrogen screen (YES) and yeast androgen screen (YAS) procedures, a genetically modified strain of *Saccharomyces cerevisiae* is used to detect and signal the presence of estrogen/androgen agonists and antagonists in environmental samples, wastewater, sludge, etc. A degree of sample preparation is required. The YES (Routledge and Sumpter, 1996) is a reporter-gene assay in which β -galactosidase is produced by the genetically modified yeast strain in the obligate presence of estrogenic compounds. The human *hER- α* gene was used to transform the yeast genome, where it is expressed constitutively. After an estrogen agonist or antagonist enters the yeast cell, it combines with the *hER- α* estrogen receptor protein, forming a complex that binds to the plasmid-borne estrogen receptor element (ERE) leading to transcription/translation of the reporter gene, here *β -gal*. β -galactosidase so produce is capable of cleaving chlorophenol red- β -galactopyranoside (CPRG) into chlorophenol red and galactose. The concentration of the red dye so produced is determined colorimetrically at $\lambda = 570\text{nm}$ after a specified incubation period in the presence of CPRG and compared to a set of standards to determine whole-sample estrogenic activity. YAS procedures are entirely parallel. Differences between the tests arise from the nature of the genetic modifications to the test organism only. Anti-estrogen and anti-androgen activities can be determined via modest modification of the original procedures (Sohoni and Sumpter, 1998).

Structural differences between the cell envelopes of human and yeast cells and differences in cofactors used for gene expression, have motivated skepticism regarding the applicability of the YES/YAS procedures for determining exogenous stimulation or repression of endocrine regulated activities in fish or humans. Reservations have largely been set aside, however, by direct comparison of the YES/YAS response to known estrogen/androgen agonists with the responses of alternative, mammalian cell assays. Although the YES/YAS procedures are less sensitive than mammalian cell bioassays, this shortcoming is overcome by concentrating samples prior to measurements and more than compensated for by relative procedural simplicity and cost reduction. All of these tests suffer from a singular shortcoming, however, in that each responds only to compounds that are capable of binding to respective steroidal hormone receptor proteins. Other forms of endocrine system disruption cannot be detected in this way.

CEC Analytical Methods

Sample collection and preparation

All samples were collected in pre-cleaned and muffled amber glass bottles. Trace organics were extracted within 24 hours. Samples were filtered through 0.7 µm PALL glass fiber filters, deuterated internal standards were added and then the samples were extracted using Waters Oasis HLB SPE cartridges. HLB sorbents were conditioned with 5 ml of MeOH, 5 ml of MTBE and 5 ml of water. One-half g of EDTA was dissolved in one liter of each source water sample before it was loaded onto the SPE sorbent at 10 ml min⁻¹. Sorbents were dried with N₂ for 40 min before sorbates were sequentially eluted with 3 ml of MeOH, 3 ml of 5% NH₄OH in MeOH, 3ml of ACN and 3ml of MTBE. The combined eluents were evaporated to about 50 µl and re-dissolved in 1 ml 50% aqueous methanol for LCMS analysis.

Analytical

An Agilent 1290 Infinity LC System coupled to an Agilent 6460 Triple Quadrupole LC/MS system using both positive and negative electrospray ionization was used for analysis of CECs (Table 2). Calibration standards were obtained from Sigma Aldrich, except for perfluorohexadecanoic acid (PFHxDA) which was obtained from Matrix Scientific, meprobamate from Cerilliant, and triclosan from Alfa Aesar. Calibration standard solutions were prepared by first making 500ug/mL stock solutions of each standard from the neat solid in HPLC pesticide grade methanol. Subsequent calibration and fortification solutions were prepared by mixing of all standards in methanol at 10ug/ml, followed by successive dilution to obtain the required concentrations. Labeled internal standards were used whenever available, and were purchased from Cambridge isotope laboratories with the exception of 13C4-PFOA, 13C4-PFOS, 13C2-PFHxA, 13C4-PFBA (Wellington Laboratories), 13C6-diclofenac, primidone d5 (Toronto Research Chemicals), and gemfibrozil-d6 (C/D/N) isotopes. All solvents used were of the highest purity available. Methyl tertiary- butyl ether (MTBE), formic acid and ammonium hydroxide were obtained from Fisher Scientific, while acetonitrile and methanol were obtained from Burdick and Jackson.

Table 2. Listing of the 36 CEC analytes that were assessed in the SCR sediments. (Asterick = known endocrine disrupting compound.)

Atenolol	PFBS
Atrazine	PFDA*
Benzophenone*	PFDoA*
Benzotriazole (BTA)*	PFHxDA
Bisphenol A (BPA)*	PFOA*
Caffeine	PFOS*
Carbamezapine	Prednisone
DEET	Primidone
Dexamethasone	Propylparaben*
Diclofenac	Simazine
Diphenylhydramine	Sucralose
Ditiazem	Sulfamethoxazole
Fluoxetine	TCEP
Gemfibrozil	TCPP*
Ibuprofen	Testosterone*
Meprobamate	Triclocarban (TCC)*
Naproxene	Triclosan*
Norgestrel	Trimethoprim (TMP)

c. PRINCIPAL FINDINGS AND SIGNIFICANCE

Estrogenic activity

The concentration of estrogenic activity in secondary effluent discharged from the Roger Rd WWRF into the Santa Cruz River ranged from 1.1 to 1.6 nM EE2 equivalents/L (300 to 450 ng EE2/L) ([Figure 3](#)), well above the levels known to elicit serious physiological disruption to any exposed fishes. Since this effluent contains relatively high levels of ammonia nitrogen (on the order of 20-25 mg NH₃ per L), fish populations at present in the lower SCR are essentially nonexistent. [Figure 4](#) shows a comparison of results from the June 22, 2012 sample set for suspended solid and liquid phase components of estrogenic activity during transport along the 37-km reach of the effluent-dependent lower SCR. About 20% of the total estrogenic activity (corresponding to 0.4 nM EE2 equivalents/L (110 ng EE2 equivalents/L) resided in the suspended solid component of the effluent discharged from the Roger Road reclamation facility ([Figure 4](#)). It is anticipated that the loading rate of estrogenic activity from the Roger Rd WWRF point source will decrease substantially following completion in 2015 of an upgraded reclamation facility at this location.

For all three sampling events during 2012, the concentration of estrogenic activity in the SCR decreased dramatically during transport downstream from Roger Rd., with both the liquid phase and suspended solid components decreasing by more than 95% after about 7.2 km travel distance downstream from the Roger Rd. outfall ([Figures 3 and 4, respectively](#)). It was not possible to assess removal mechanisms of estrogenic activity during this study but responsible processes could include biodegradation, photolysis, and/or settling/sorption to riverbed sediments.

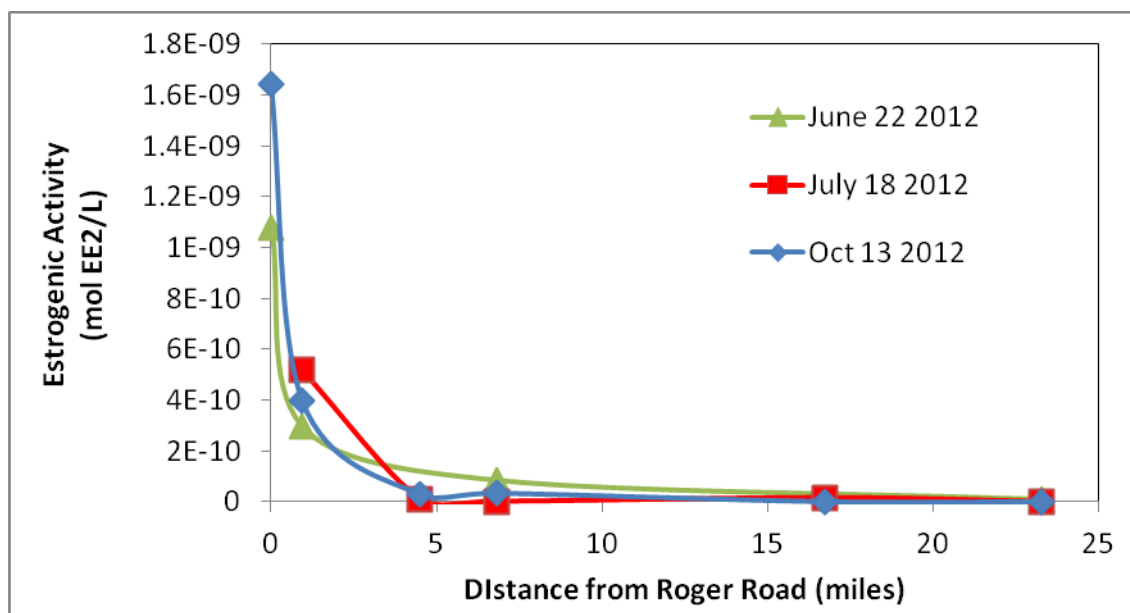


Figure 3. Liquid-phase concentrations of estrogenic activity (moles of EE2 equivalents/L) in water samples collected along the lower Santa Cruz River, Arizona (mile 0 = Roger Rd. outfall).

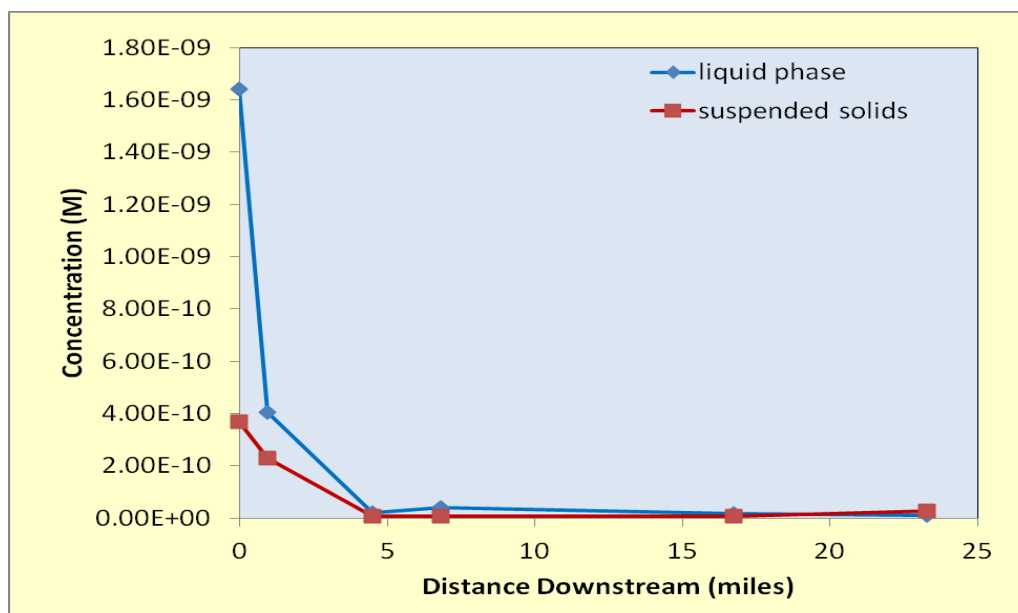


Figure 4. Comparison of estrogenic activity concentrations (moles of EE2 equivalents/L) for the liquid phase and suspended solid sample components along the lower Santa Cruz River, Arizona on June 22, 2013 (mile 0 = Roger Rd. outfall).

Estrogenic activity was detected in some of the 0-5cm depth sediment extracts (Figure 5). The detection limit for estrogenic activity in riverbed sediments was estimated at 2.84×10^{-13} M EE2 equivalents/L. Estrogenic activities were highest in the pre-monsoon (June 22, 2013) surface sediment samples collected at the Cortaro Rd. (6.8 mi) and Trico Rd. (23.8 mi) sampling sites. Estrogenic activity in sediments from these locations was much reduced, or nondetectable, in the

two post-monsoon (July 18, October 13) sediment sample sets. These data are consistent with a scenario in which near-surface bed sediments along the study reach are scoured and transported downstream during high flow runoff events in summer, replaced by newly deposited sediments originating from upstream of the Roger Rd. outfall and presumably possessing little or no estrogenic activity (dry riverbed except during storm runoff events). This would thus represent an annual cycle of scour of “contaminated” sediment followed by deposition of relatively cleaner sediment along the effluent-dependent study reach.

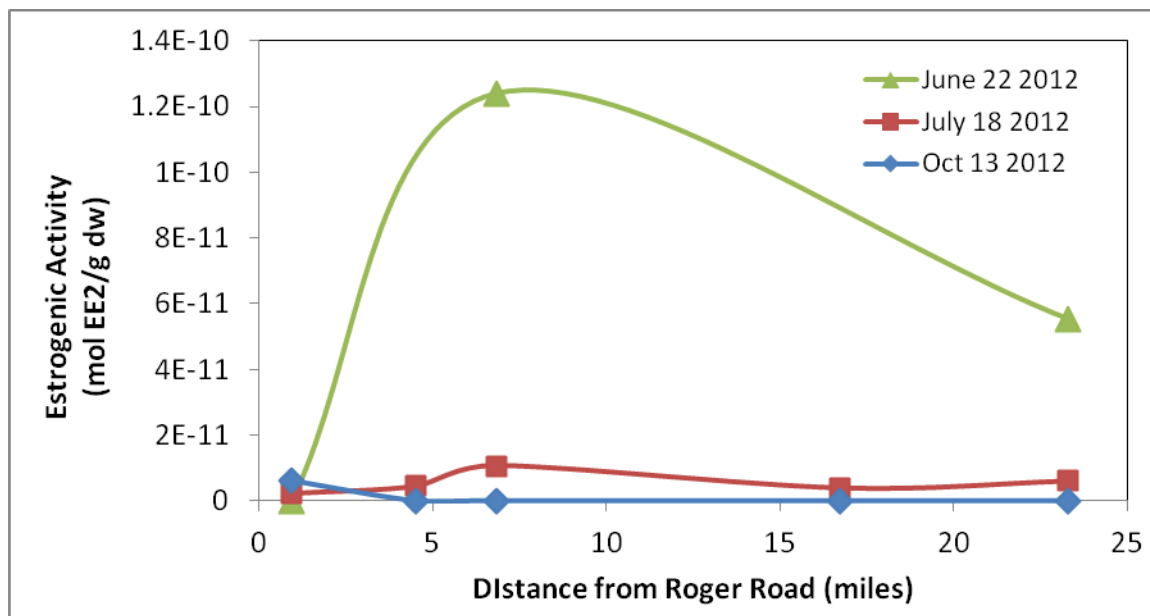


Figure 5. Sediment-bound concentrations of estrogenic activity in the 0-5cm depth sediment samples collected from the lower SCR (mile 0 = Roger Rd. outfall).

Androgenic Activity

Liquid-phase, suspended solid, and sediment extracts were all analyzed for androgenic activity using the YAS bioassay. Suspended solid and sediment extracts all tested negative for androgenic activity. A very small minority of liquid-phase river samples showed very small detections for YAS that could not be reliably quantified.

Chemicals of Emerging Concern

A fourth set of sediment samples was collected along the lower SCR in February 2013 and tested for a suite of thirty six CECs (Table 2). Sixteen of these CECs were detected in the (upstream) sediment sample nearest the Roger Rd outfall; of these, eight CECs (caffeine, TCPP, benzotriazole, triclocarban, trimethoprim, benzophenone, bisphenol A, and triclosan) were detected in sediment extracts obtained from all six riverbed sampling locations (Figure 6) with concentrations ranging from sub parts per billion upwards to almost 100 ppb. Known endocrine disruptors that were detected at the majority of sediment sampling sites included benzophenone, benzotriazole, bisphenol A, TCPP, triclocarban, and triclosan.

The CEC detected at greatest concentration in SCR sediments was caffeine; this result was somewhat unexpected given the modest K_{ow} value for caffeine ($\log K_{ow} = 0.01$). Although there were notable exceptions, sediment-bound CEC concentrations (ng/g) were generally highest towards the upstream sampling sites and decreased as a function of downstream distance (Figure 6).

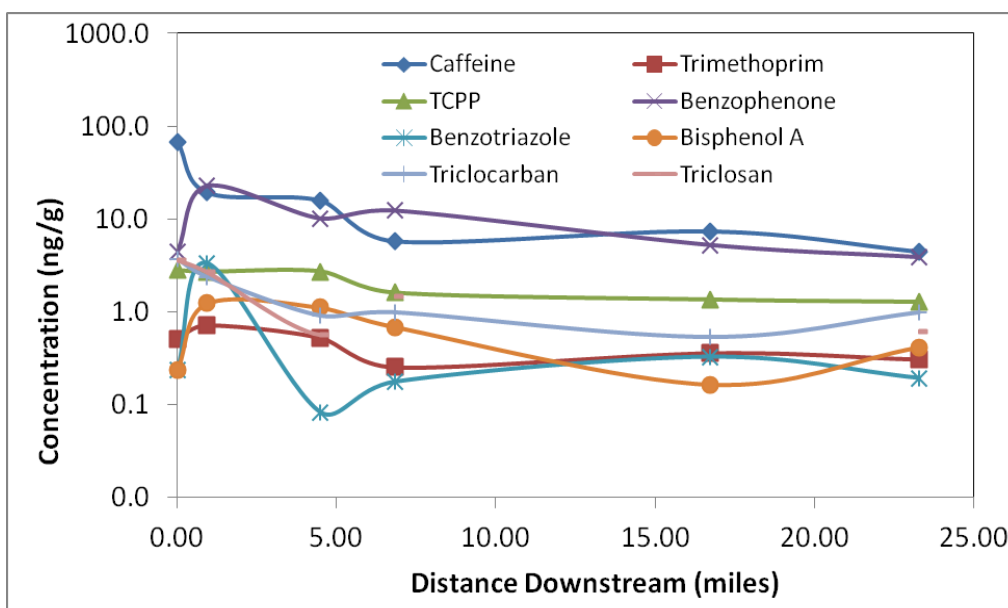


Figure 6. Concentrations (ng/g) of the eight CECs detected at all six SCR sediment sampling locations along the 23-mile (37-km) reach of the lower SCR (mile 0 = Roger Rd. outfall).

Summary of Findings:

Many chemical of emerging concern (CECs) that enter municipal wastewater through domestic use are only partially removed during conventional wastewater treatment. Many of these are innocuous in character (e.g. cholesterol) but they also include endocrine disrupting compounds (EDCs), such as estrone and other estrogenic compounds, at concentrations that are potentially deleterious to continuously exposed aquatic organisms residing downstream from discharge points of municipal effluent. In addition, EDCs and other CECs may accumulate in riverbed sediments via deposition of suspended solids or sorption of liquid-phase CECs during effluent infiltration/percolation in the riverbed. We evaluated the occurrence and fate of EDCs, measured as estrogenic activity, along a 23-mile reach of the Lower Santa Cruz River (SCR) as a function of distance downstream from municipal wastewater reclamation facilities in Tucson. River water, suspended solids, and riverbed sediments were sampled to establish the persistence of toxicity in river/sediments. Sampling was performed before and after the 2012 summer monsoon rainstorm season to assess associated impacts on sediment-bound endocrine disruption activities as consequence of increased river flow rates during summer runoff events. Liquid-phase and suspended solid concentrations of estrogenic activity decreased by more than 95% during in-stream transport along the 23-mile reach of the SCR. Estrogenic activity concentrations in near-surface sediments were found to be highest in the pre-monsoon riverbed samples. Presumably, these sediments were scoured and transported downstream during high runoff events in summer,

replaced by newly deposited (upstream) sediments possessing little or no estrogenic activity. This would thus represent an annual cycle of scour of “contaminated” sediment followed by deposition of relatively cleaner sediment in the riverbed along the effluent-dependent study reach.

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Information Transfer Program Introduction

The WRRC's information transfer program is designed to meet the need in Arizona for objective, accessible and usable water resources information. The program consists of regular and occasional publications, an annual conference, a brown bag seminar series and additional events and activities. Use of electronic media has increased and is extending the reach of the program. Strategic planning has placed renewed emphasis on collaborations and partnerships in developing projects and programs of research and outreach. The Environmental Programs and Desert Water Harvesting projects are collaboratively based. In addition to direct public outreach activities, they include access to resources through dedicated web sites located within the WRRC site. The WRRC-based Arizona Project WET has expanded its education activities for teachers and students throughout the state, including its interactive in-service workshops, Water Festivals, and initiatives in inquiry-based water education such as the Water Investigations Program.

Public interest water issues remains high in Arizona, particularly issues associated with water sustainability, climate variability and change, water harvesting, environmental water needs, statewide water planning, and water reuse.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2012AZ501B
Start Date:	3/1/2012
End Date:	2/28/2013
Funding Source:	104B
Congressional District:	AZ007
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Focus Category:	Law, Institutions, and Policy, Management and Planning, Economics
Descriptors:	None
Principal Investigators:	Sharon Megdal, Susanna Eden, Jean E.T. McLain

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The WRRC's Information Transfer Program has continued to produce its major component products in the project year. These include the Arizona Water Resource (AWR) and Arroyo newsletters, the Annual Conference, Brown Bag seminars, and the website. Collaborations continue with the Water Sustainability Program, now a part of the Water, Environmental and Energy Solutions Initiative, and with Arizona Project WET.

Events

Annual Conference

The WRRC's Annual Conference for 2012 was held January 24, in collaboration with the Arizona State University, Morrison Institute for Public Policy. The conference, "Urbanization, Uncertainty and Water: Planning for Arizona's Second Hundred Years," took place at the UA Memorial Student Union. Collaboration with the Morrison Institute on the conference followed release of their report, "Watering the Sun Corridor: Managing Choices in Arizona's Megapolitan Area." The conference broadened the focus beyond the ASU report, to encompass the whole state. Two other contemporary reports were featured: "Arizona at the Crossroads: Water Scarcity or Water Sustainability," published by the Grand Canyon Institute, and the Final Report of the Water Resources Development Commission (WRDC). Approximately 330 participants attended from 40 communities across Arizona. A half-day workshop on water sustainability in the Sun Corridor, sponsored by the Sonoran Institute and the Lincoln Institute of Land Policy and held in conjunction with the conference, attracted 60 participants. Thirteen external sponsors contributed to support of the conference.

Planning and organization for the 2013 Annual Conference proceeded throughout 2012. Organized in collaboration with the U.S. Geological Survey, Water Science Center, the conference program focused on water security. Scheduled for March 5, 2013, at the University of Arizona, "Water Security from the Ground Up" employed broad definition was water security ensuring that a range of issues from sustainability of water supplies and protection of water quality to policy tools for water governance would be address by invited speakers. More than 300 people registered for the conference. External sponsors include utilities, consulting firms and nonprofit organization.

Brown Bag Seminars

The WRRC expanded its series of Brown Bag Seminars to fulfill demand for information on water-related topics of current interest. The Brown Bag Seminars provide a forum for researchers, students and community members to learn about and discuss water resources issues. The WRRC's brown bag seminar series offers information and opportunities for two-way dialogue and for community-university interaction. Seminars focus on topics of broad interest to academics from multiple disciplines and members of the water and related resource communities. Eighteen Brown Bags were held in the project year. Average attendance was 25 people, with about 40 percent representing the community and 60 percent from the University. Dates and titles of the Brown Bags from March 1, 2012 through February 29, 2013 are listed below:

- *March 21, 2012; Monica Ramirez-Andreotta, M.P.A., Ph.D. Candidate, Department of Soil, Water and Environmental Science, University of Arizona; Gardenroots: The Dewey-Humboldt, Arizona Garden Project*
- *April 19, 2012; Rosalind Bark, Ph.D., CSIRO Ecosystem Sciences, Australia; Valuing the multi-benefits of the Murray-Darling Basin Plan using an ecosystem service framework*
- *April 26, 2012; Anthony (Tony) Willardson, Executive Director, Western States Water Council; Water Needs and Strategies for a Sustainable Future: Managing Uncertainty*
- *May 9, 2012; Joanna Nadeau, Research Analyst, Water Resources Research Center, University of Arizona; Exploring Strategies for Managing Water and the Environment in an Arid Land*

- *May 17, 2012; Tony Sedgwick, landowner and 2012 recipient of the National Wetlands Award for Landowner Stewardship; President of Santa Fe Ranch; Las Lagunas de Anza - The story of the transformation of a dump into lovely wetlands in the City of Nogales, Arizona*
- *August 24, 2012; Debbie Colodner, Director of Conservation Education and Science, Arizona-Sonora Desert Museum; Kerry Schwartz, Arizona Cooperative Extension Associate Specialist and Director, Arizona Project WET, WRRC, University of Arizona; Sanlyn Buxner, Education Specialist, College of Education and Planetary Science Institute, University of Arizona; Power of Perspective: Using NASA Data to Engage Teachers, Students and the Public in Learning about Planet Earth through Earth Camp Programs*
- *September 5, 2012; Jennifer McCloskey, Area Manager, Bureau of Reclamation, Yuma Area Office; Managing the Colorado River: A Balancing Act*
- *September 25, 2012; Peter Dillon, Stream Leader, Sustainable Water Solutions Urban Water Theme, Water for a Healthy Country Flagship Program, CSIRO Land and Water, Glen Osmond, SA, Australia; Governance measures to effectively manage groundwater storage*
- *October 17, 2012; Val Little, Director, Water CASA; INT-N-EXT Water Use Study, Tucson*
- *November 14, 2012; Dr. Kim Ogden, Professor, UA Department of Chemical & Environmental Engineering; Biofuel Production and Water in the Southwest*
- *November 16, 2012; William L. Andreen, Edgar L. Clarkson Professor of Law, University of Alabama School of Law; Success and Backlash: The Remarkable (Continuing) Story of the Clean Water Act*
- *November 20, 2012; Arizona Cooperative Extension 2012 Summer Externs (Jessica Ackley, Jill Hamilton, Madalyn Hemminghaus, Erika LaPlante, Bakbergen Turibekov); 2012 Summer Extern Update: County Sustainability Projects that Improve the Lives of Arizonans*
- *November 29, 2012; Sharon Megdal, Director, Water Resources Research Center, Specialist and Professor, Department of Soil, Water and Environmental Science, The University of Arizona; Searching for Water Solutions: Experiences from My Sabbatical and Other Travels*
- *December 6, 2012; Emily Brott, Sonoran Institute; Lisa Shipek, Watershed Management Group; Candice Rupprecht; WRRC; Tucson Conserve to Enhance Workshop for Funding Local Enhancement Projects*
- *January 31, 2013; Pablo Garcia-Chevesich, Researcher at the Forest Institute of Chile; Land Reclamation on Easter Island*
- *February 8, 2013; Lisa M. Beyer, RLA, Landscape Architect at AECOM Water in San Francisco, On-site consultant to the San Francisco Public Utilities Commission; Rethinking Water Infrastructure: Philadelphia and San Francisco's Approaches to Implementing Green Stormwater Infrastructure Programs*
- *February 20, 2013; Jeff Lukas, Senior Research Associate, Western Water Assessment, University of Colorado – Boulder; Paleohydrology of the Lower Colorado River Basin and Implications for System Risk*
- *February 27, 2013; Professor Nir Becker, Department of Economics and Management, Tel-Hai College, University of Haifa; Israel Rivers restoration in Israel: A sustainable economic approach to measure non-market values in a trans-boundary setting*

Other Outreach Events

Additional outreach events warrant special attention owing to their high attendance and impact:

On Saturday, April 14, the WRRC's Conserve to Enhance program cosponsored a visit to the Atturbury Wash restoration project, the site chosen to receive Conserve to Enhance donations. Naturalist Eric Dhruv led a 90-minute plant walk in and around the wash.

On September 19, 2012, the WRRC co-hosted a screening of the movie WATERSHED, a documentary produced by the Redford Center. Narrated by Robert Redford and directed by award-winning filmmaker, Mark Decena, WATERSHED tells the story of the threats to the Colorado River and suggests actions that can be taken to protect and restore it. The film was followed by a panel discussion that explored the Colorado River Basin's water supply challenges. The film and following discussion focused attention on the river's delta ecosystem. Panelists described the current state of Delta ecosystem, the need to restored flows and restoration work that is already being done. The panel concluded with what is being done in our community to conserve water and create this new water ethic. The event took place at the Loft Cinema in Tucson, Arizona, co-hosted with the Sonoran Institute.

The WRRC co-hosted a delegation from La Paz, Baja California Sur, Mexico, October 28-30, 2012. The delegation visited Tucson and Phoenix to learn about water and utilities management in our region. La Paz, Mexico is a participant in the Emerging Sustainable Cities Initiative of the Inter-American Development Bank (IDB).

Grey Water Workshop was held October 1-4, 2012: at the WRRC to plan future collaborations with researchers at the Jordanian Royal Scientific Society. Presentations were made by the Jordanians and Arizona grey water experts at a pre-workshop meeting attended by interested members of the Arizona water community.

On October 23, 2012, WRRC hosted the Statewide Water Conservation Infoshare meeting at the WRRC, cosponsored by WRRC and WSP. The Infoshare group is made up of water conservation staff from municipalities, utilities, and other agencies. A field trip to Sweetwater Wetlands followed the program.

A new Water Sustainability Distinguished Speaker Series was initiated in early 2013 by the Water Sustainability Program in cooperation with the WRRC. The speaker series included a presentation on February 5 by Justice Gregory Hobbs, Colorado Supreme Court, and a talk by Patricia Mulroy, General Manager, Southern Nevada Water Authority on February, 28, 2013.

Every year the WRRC hosts a "Chocolate Fest" in February for friends of the WRRC. In 2013, the Fest was held on February 15, and featured two significant events. A book launch was held for the newly published *Shared Borders Shared Waters, Israeli-Palestinian and Colorado River Basin Water Challenges*, edited by the WRRC's Sharon B. Megdal and Susanna Eden, and Robert G. Varady of the Udall Center for Studies in Public Policy. In addition, winners of the WRRC's photography contest, "Water, the Human Element," were announced and the winning photographs were displayed. The event was well-attended by University faculty, students and friends from the community.

Newsletters

Arizona Water Resource Newsletter (AWR)

Published by the WRRC since 1993, the AWR newsletter appears quarterly. With a new look and under a new editorial system, the highly regarded newsletter continued as a keystone of the WRRC's Information Transfer program. The AWR is an 8 to 12-page newsletter focusing on state and regional water issues. In 2012 new procedures were put in place to develop a greater percentage of articles by external authors and by Graduate Outreach Assistants. The template for the newsletter has been refined yielding a cleaner look and greater ease of layout. Published quarterly, the print version is sent free of charge to approximately 2,000 subscribers. In addition an electronic version is available on-line and emailed to more than 10,000 subscribers. The AWR has wide distribution; the majority of its readers are from Arizona, but it also is mailed to other states and foreign countries. The publication regularly includes feature articles, a guest view, news briefs, sections on special projects, as well as announcements and publication notices. A public policy column, written by the WRRC Director, regularly receives attention and comment as a

leading source for water policy analysis. Many issues of the newsletter include a four-page special supplement. In Summer 2012, the Water Sustainability program sponsored a supplement of program highlights, and the U.S. Geological Survey sponsored the supplement “Understanding and Managing the Effects of Groundwater Pumping on Streamflow,” in the Winter 2013 issue.

A listing of the key feature articles for each of the four 2012 newsletters appears below:

Winter 2013

- New Members Share Thoughts about Goals for CAWCD Board
- National Climate Assessment Foresees Alarming Impacts on Southwest

Fall 2012

- Food Safety Concerns Drive Research
- Building Bridges, Wetlands, and Water Sustainability: Lessons from an Arizona-Baja California Sur Partnership

Summer 2012

- STEM Refocuses Water Education in Arizona
- The Water Investigations Program Inspires Tomorrow’s Scientists and Engineers

Spring 2012

- Mexico Visit Strengthens Understanding of Shared Environmental Interests
- Arizona and the Southwest Face Heightened Fire Threat

Arroyo

An annual newsletter that presents in-depth discussion of a single topic, *Arroyo* addressed “Border Water as Source of Conflict and Cooperation” in Arizona in the 2012 issue. The U.S-Mexico border is not only where two countries meet, but where different cultures face a common need for effective and sustainable use of the available resources. Agencies from both countries are addressing the challenge by participating in binational efforts to resolve the issues of water and air contamination, water resource allocation, and solid and hazardous waste disposal in the region.

The 2013 *Arroyo* covers water contaminants of emerging concern (CECs). Topics are chosen by the WRRC’s External Advisory Committee. The topic chosen for the 2014 *Arroyo* is “The Value of Water”.

An internship, sponsored by Montgomery & Associates, a water resources consulting firm, supports initial research for the *Arroyo*. The intern, who is selected through a competitive process, conducts research, including interviews of key experts, and creates drafts for the *Arroyo*. In 2012, the intern was Radhumitha Raghav, whose research on CECs was the basis of the 2013 *Arroyo*. Montgomery & Associates has sponsored the summer interns since 2008.

Both publications are available free on-line or by subscription. Strategic planning examined the possibility of phasing out print publication of the *AWR* and *Arroyo*, but the popularity of the print format among the WRRC’s stakeholders has caused us to put any such plans on hold for the foreseeable future. Efforts are underway to increase external support for printing the newsletters.

Web Site

The WRRC makes extensive use of our web site. In addition to WRRC news and events, the site carries *AWR* and *Arroyo*, as well as papers, presentations and links to other water related sites. The site also offers a calendar and comprehensive information about WRRC activities such as the Annual Conference, the Brown Bag Seminar series, the Summer Internship competition and the 104(b) Research Grants Program. Staff profiles and information about WRRC products also are easily accessible.

The WRRC web site underwent a complete redesign to update the look and improve navigability. Updates take advantage of DRUPAL (an open content management system) modules and demonstrate consistency with the UA brand. Web management protocols call for continuous evaluation of the website to improve its efficiency and effectiveness. Web posts are updated frequently. Registration for the WRRC conference is made available through the web site. The site also includes pages of information, forms and documents associated with specific WRRC programs. These include pages for Environmental Programs, the Conserve to Enhance Program and the Desert Water Harvesting Initiative. A website for the Arizona component of the U.S.-Mexico Transboundary Aquifer Assessment Program is supported by the WRRC and linked through the WRRC website. Links to the Water Sustainability Program and Arizona Project WET website are also provided.

In keeping with general trends in communication, the WRRC is placing increasing emphasis on the internet as a public information tool. A half-time information and communication specialist, hired in January 2013, works closely with the WRRC's web manager to enhance external communications. Recent changes focus on timely updating of feature stories on the web site and email notifications using Constant Contact in a visually attractive format. The information and communication specialist also coordinates media relations and other publicity for WRRC events and activities. The WRRC Facebook presence is growing with increased attention to keeping posts fresh and interacting with the on-line community.

Other Information Transfer

Ongoing programs of research and outreach continued and expanded. A program that provides information on environmental water needs to support watershed planning has continued to expand across Arizona watersheds and is developing a "roadmap" to environmental participation in water planning. Several projects are underway designed to fill data gaps for communities interested in implementing water harvesting as a strategy with multiple benefits. Under the umbrella of the Desert Water Harvesting Initiative, these projects focus on the expressed needs of water managers and planners. Water managers and others concerned with groundwater management under climate change have been engaged in the development and use of a groundwater modeling scheme. These grant funded programs have received some services from the Information Transfer Program.

In addition to the above programs, publications and events, WRRC personnel continued their public service activities. They were called upon regularly to give lectures and make presentations to diverse audiences across Arizona. WRRC personnel participate on community and regional boards and commissions, serve on state and local task forces and study committees, and regularly attend important water resources meetings. In addition, the WRRC continued to extend its information transfer role through collaboration with the university-wide Water Sustainability Program, a component of the Water, Environmental and Energy Solutions (WEES) initiative. The WRRC Director serves as one of two co-Directors of WEES.

WRRC personnel also responded to inquiries from the public on issues of concern. Topics of particular concern in the project year included water sustainability, climate variability and change, water harvesting, environmental water needs, statewide water planning, and water reuse.

Presentations by 104b and 104g Project Personnel

"Does Increasing Solids Retention Time in the Wastewater Treatment Process Affect the Persistence of Antibiotic Resistance Genes?" (Project 2012AZ478B)

- Walston, S., J.E.T. McLain, L. Abrell, D. Gerrity, and C.M. Rock (2012) Poster: Does Increasing Solids Retention Time in Wastewater Treatment Plants Affect the Persistence of Antibiotic Resistance Genes? American Society for Microbiology (ASM) Annual Conference.
- Walston, S., J.E.T. McLain, L. Abrell, D. Gerrity, and C.M. Rock (2012) Poster: Does Increasing Solids Retention Time in Wastewater Treatment Plants Affect the Persistence of Antibiotic Resistance Genes? EARTH WEEK 2012 Soil, Water & Environmental Science Student Showcase.
- Walston, S., J.E.T. McLain, L. Abrell, D. Gerrity, and C.M. Rock (2012) Does Increasing Solids Retention Time in Wastewater Treatment Plants Affect the Persistence of Antibiotic Resistance Genes? AZ Water 85th Annual Conference & Exhibition.
- Rock, C.M., S. Walston, J.E.T. McLain, L. Abrell, and D. Gerrity (2012) Does Increasing Solids Retention Time in Wastewater Treatment Plants Affect the Persistence of Antibiotic Resistance Genes? National Science Foundation (NSF) Water Quality Center Annual Meeting.
- Rock, C.M., S. Walston, J.E.T. McLain, L. Abrell, and D. Gerrity (2012) Does Increasing Solids Retention Time in Wastewater Treatment Plants Affect the Persistence of Antibiotic Resistance Genes? Institute of the Environment: Grad Blitz 2012

Fate of Emerging Nanoparticle Contaminants during Aquifer Recharge with Treated Wastewater (2012AZ476B)

- Rottman, J., L. Platt, R. Sierra-Alvarez, F. Shadman. 2012. Poster: Measurement and Retention of Nanoparticles in Semiconductor Processing Effluents using Porous Media Filtration. Annual Meeting SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing Review. March 20-22, Tucson, AZ.

Fate of Emerging Contaminants in an Effluent Dependent Stream: the Role of Suspended Solids and Sediments (2012AZ492B)

- Quanrud. "Fate of emerging contaminants along the Lower Santa Cruz River, Arizona." Presented at *Friends of the Santa Cruz River Researchers Day*. Tucson, Arizona, March 29, 2012.

Improving Hydrologic Investigations through Multi-Model Analysis and Discriminatory Data Collection (2010AZ412G)

- Kikuchi, C.P., T.P.A. Ferre, T. Bayley, S. Hundt. 2012. Discrimination-Inference to Reduce Expected Cost Technique: Application to groundwater-surface water investigations. American Geophysical Union Fall 2012 Meeting, Invited Talk, Dec. 3-7.

Presentations by WRRC Personnel

March 18, 2012, Megdal, Sharon B., Presentation, Arizona and Israeli Water Policy: Some Similarities and Differences, Department of Agricultural Economics and Management Seminar, The Hebrew University of Jerusalem, Rehovot, Israel.

March 22, 2012, Megdal, Sharon B., Presentation, Overview of Arizona Water Management, Arava Institute, Israel.

March 26, 2012, Megdal, Sharon B., Introduction to Arizona Water Resources, Massar High School Environmental Science Class, Lilian Daniel, Instructor, Nazareth, Israel.

March 28, 2012, Nadeau, Joanna, Assessing the Role of the Environment as Water Customer, The International Symposium of the Flora of Arid Zones; Gomez Palacio, MX.

March 29, 2012, Eden, Susanna, Session co-organizer, Developing a Southwestern Research Agenda for Rainwater and Stormwater Harvesting Methodologies for Green Infrastructure and Low Impact Development, AridLID Conference, Tucson, AZ.

March 29, 2012, Lien, Aaron, Conserve to Enhance: a tool for linking green infrastructure, water conservation, and consumer education, AridLID Conference, Tucson, AZ.

March 30, 2012, Mott Lacroix, Kelly, Connecting the Environment to Arizona Water Planning, Arizona Riparian Council Meeting, Safford, AZ.

April 18, 2012, Nadeau, Joanna, Connecting Environmental Water Needs to Arizona Water Planning, SW Tribal Climate Change Network Call.

April 18-20, 2012, Megdal, Participant and Session Rapporteur, GEF Project “Groundwater Governance: A Global Framework for Country Action” UNESCO First Regional Consultation: Latin America and the Caribbean Region, Montevideo, Uruguay.

April 21, 2012, Schwartz, Kerry, (with Arizona-Sonora Desert Museum) NASA Earth Camp Educator Workshop.

April 26, 2012, Lien, Aaron, C2E, Carpe Diem West Healthy Headwaters Working Group, Phoenix, AZ.

April 26, 2012, Megdal, Sharon B., Meeting Arizona’s future water demands under decentralized governance, CSIRO, Adelaide, South Australia.

April 27, 2012, Rupprecht, Candice, C2E and EnWaP projects, Coconino Plateau Water Advisory Committee, Flagstaff, AZ.

April 27, 2012, Megdal, Sharon B., The Importance of Institutional Asymmetries to the Development of Binational Aquifer Assessment Programs: The Arizona-Sonora Experience, The Centre for Comparative Water Policies and Laws, The University of South Australia, Adelaide, South Australia.

May 1, 2012, Mott Lacroix, Kelly, Assessing and Addressing Ecological Water Needs in Arizona, Madrean Conference, Tucson, AZ.

May 1, 2012, Megdal, Sharon B., Water Banking and Groundwater Management in Arizona, CSIRO, Canberra, ACT, Australia.

May 2, 2012, Megdal, Sharon B., Water Banking and Groundwater Management in Arizona, Murray-Darling Basin Authority, Canberra, ACT, Australia.

May 2-4, 2012, Mott Lacroix, Kelly, Environmental Water Demands and Water Planning, Arizona Water Association Conference, Phoenix, AZ.

May 2-4, 2012, McLain, Jean, Establishing the public health safety of recycled municipal wastewater: current research, Water and Wastewater Management Summit, Las Vegas, NV.

May 9, 2012, Nadeau, Joanna, Exploring Strategies for Managing Water and the Environment in an Arid Land, Water Resources Research Center Brownbag Seminar, Tucson, AZ.

May 14, 2012, dos Santos, Plácido, [La](#) Gestión del Agua en el Estado de Arizona (Water Management in the State of Arizona.) For visitors from the Universidad Autónoma de Chapingo, Durango, Mexico. Water Resources Research Center, Tucson, AZ.

May 14, 2012, dos Santos, Plácido, El Reciclaje y la Recarga de Aguas Residuales Tratadas en Arizona (The Reuse and Recharge of Treated Wastewater in Arizona.) For visitors from the Universidad Autónoma de Chapingo, Durango, Mexico. Water Resources Research Center, Tucson, AZ.

May 20-24, 2012, McLain, Jean, panelist, Water recycling, reuse, and sustainability: the need for a new water supply paradigm, National Water Conference in Portland, OR.

May 20, 2012, Nadeau, Joanna, Conserve to Enhance, Association of Natural Resources Environmental Professionals (ANREP) Biannual Conference, Hendersonville, NC.

May 30, 2012, Schwartz, Kerry, (with Arizona-Sonora Desert Museum), NASA Earth Camp Educator Workshop, Tucson, AZ.

June 1, 2012, Megdal, Sharon B., General Rapporteur, Expert Workshop on Water Security: Managing Risks and Tradeoffs in Selected River Basins, Organization for Economic Co-operation and Development Working Party on Biodiversity, Water and Ecosystems, OECD, Paris, France.

June 4, 2012 Candice Rupprecht, Water and Its Impact on People, Planet, and Profit, Tempe USD Sustainability Conference, Tempe, AZ.

June 4, 2012, Megdal, Sharon B., Scientific cooperation in water sciences. Science, Networks, Consciousness in the Mediterranean Basin, organized by the French Academy of Sciences and UNESCO, UNESCO, Paris, France.

June 4, 2012, Megdal, Sharon B., Panelist, Science, Networks, Consciousness in the Mediterranean Basin, organized by the French Academy of Sciences and UNESCO, UNESCO, Paris, France.

June 6, 2012, Cleveland, Jenna, Anne Audrey, Jackie Moxley, Susanna Eden, WaterSmart water harvest assessment tool, Arizona Municipal Water Users Association, Tucson, AZ.

June 6, 2012, McLain, Jean, Exploring Environmental and Public Health Impacts of Reclaimed Water: Is It Safe?, Pinal County Cooperative Extension, Tucson, AZ.

June 8, 2012, Megdal, Sharon B., Co-presenter (with James Callegary), U.S.-MX Transboundary Aquifer Assessment Program Status Update, James Callegary, Christopher Scott, Sharon Megdal and Plácido dos Santos, Joint meeting of the Water Committee and the Environment Committee of the Arizona-Mexico Commission, Tucson, AZ.

June 10-14, 2012, Mott-Lacroix, Kelly, Poster Presentation, Environment in Arizona Water Planning, AWWA ACE, Dallas, TX.

June 18-22, 2012, Schwartz, Kerry, (with Arizona-Sonora Desert Museum) NASA Earth Camp Educator Workshop.

June 26-28, 2012, Schwartz, Kerry, and Candice Rupprecht, Water Investigations Program, 2012-2013 Teacher Cohort Training in Phoenix, AZ.

July 11, 2012, Nadeau, Joanna, and Kelly Mott Lacroix, EnWaP, Gila Watershed Partnership, Tucson, AZ.

July 17, 2012, Megdal, Sharon B., Perspectives on Governance and Institutions: The Search for Solutions, 2012 UCOWR/NIWR Annual Conference, Santa Fe, NM.

July 18, 2012, Megdal, Building, Maintaining and Strengthening the Bridge, Bridging Science and Application, Plenary Session, 2012 UCOWR/NIWR Annual Conference, Santa Fe, NM, co-organizer of session.

July 30, 2012, McLain, Jean, Opening Ceremony of Water Quality degree program, Centro de Investigación Científica de Yucatán (CICY) Water Sciences Unit, Mérida México.

August 9, 2012, Megdal, Sharon B., Roundtable Expert, Water Science and Management, 2012 Udall Scholar Orientation, Udall Foundation, Tucson, AZ.

August 20, 2012, Thomas-Hilburn, Holly, Water Scene Investigators, Paradise Valley, AZ.

August 27, 2012, Megdal, Sharon B., Perspectives on Governance and Institutions: The Search for Solutions, Pima Association of Governments Watershed Subcommittee, Tucson, AZ.

September 10, 2012, McLain, Jean, Minimal Production of Algal Toxins in Recycled Water Retention Ponds, 27th Annual WateReuse Symposium, Hollywood, FL.

September 12, 2012, Megdal, Presentation, The Role of Conservation in Water Management, Undergraduate Seminar for Neurosciences-Cognitive Sciences Majors, The University of Arizona, Tucson, AZ.

September 18, 2012, Cleveland, Jenna, (with Jackie Moxley and Susanna Eden), Workshop Instructor, Using Low-impact Development and Smartscape to create Sustainable Landscapes, Arizona Hydrologic Society Symposium, Phoenix, AZ.

September 19, 2012, McLain, Jean, Effective Presentation Techniques, guest lecture, SWES696a, Tucson, AZ.

September 19, 2012, Megdal, Sharon B., Panelist, Expert panel following Tucson premiere of the movie Watershed, Tucson, AZ.

September 20, 2012, Mott Lacroix, Kelly, The Environmental Water Needs Program, Arizona Hydrological Society, Tucson, AZ.

September 21, 2012, Megdal, Sharon B, Water Management and Policy in Arizona and the Colorado River Basin: Searching for Solutions, Wiseguide Luncheon, Scottsdale, AZ.

September 27-28, 2012, Megdal, Co-chair, Innovation and Water Technology Track, Binational Border Water Resources Summit: Past, Present and Future, Ciudad Juarez, Chihuahua, Mexico and El Paso, TX.

September 28, 2012, Mott Lacroix, Kelly, The Environmental Water Needs Program, Coconino Plateau Water Advisory Council, Flagstaff, AZ.

September 28, 2012, Mott Lacroix, Kelly, The Environmental Water Needs Program, Old Concho Water Users Association and Irrigation District, Concho, AZ.

September 29-30, 2012, dos Santos, Plácido, The U.S.-Mexico Transboundary Aquifer Assessment Program (TAAP): Focus on the Arizona-Sonora collaboration. The Binational Assessment of the Santa Cruz and San Pedro Aquifers, IBWC Border Water Resources Summit, El Paso, TX.

October 2012, Mott Lacroix, Kelly, Introduction to EnWaP, Environmental Engineering Seminar, University of Arizona, Tucson, AZ.

October 1-4, 2012, Megdal, Sharon B., Moderator and Host, Grey Water Use Information Exchange, Water Resources Research Center, Tucson, Arizona, October 1, 2012.

October 1-4, 2012, Schwartz, Kerry, WSI: Students Achieving Real Water Savings, Water Smart Innovations Conference, Las Vegas, NV.

October 4, 2012, Eden, Susanna, Arizona Water Resources, Green Valley Gardeners, Green Valley, AZ.

October 4, 2012, Eden, Susanna, Assessment of Decision Support Activities, guest lecture, SWES 415/515, Tucson, AZ.

October 7, 2012, Megdal, Presentation, Water Management in Arizona and the Lower Colorado River Basin: Searching for Solutions, Ministry of Water and Irrigation, Amman, Jordan.

October 8, 2012, Megdal, Sharon B., (with Robert Varady), Co-facilitator for a breakout session on "General Policies and Principles for Groundwater Governance, The GEF Project on Global Groundwater Governance: Groundwater Policy and Governance, Third Regional Consultation, GEF Groundwater Governance Project, Amman, Jordan.

October 11, 2012, Rupprecht, Candice and Brittany Choate, EnWaP and C2E, Clean Colorado River Sustainability Coalition (CCRSCo) meeting, Lake Havasu City, AZ.

October 11, 2012, Rupprecht, Candice and Brittany Choate, C2E and EnWaP, Colorado River Regional Sewer Coalition, Lake Havasu City, AZ.

October 12, 2012, McLain, Jean, co-chair (with Lynn Joens, Veterinary Science and Microbiology) and moderator, University of Arizona Food Safety Consortium Annual Meeting, Omni Tucson Resort, Tucson, AZ.

October 17, 2012, Rupprecht, Candice and Aaron Lien, Interview: Arizona Green Plumber Radio Show, Tucson AZ,
<http://www.blogtalkradio.com/thearizonagreenplumber/2012/10/17/the-arizona-green-plumber-talks-to-u-of-a-wrrc>.

October 18, 2012, Eden, Susanna, An Introduction to Incorporating Climate Information and Stakeholder Engagement in Groundwater Resources Planning and Management - A Project for NOAA Climate and Societal Interactions Sectoral Applications Research Program/Water Resource Management, Project Kickoff Workshop, Tucson, AZ.

October 20, 2012, Schwartz, Kerry, Water Investigations Program, 2012-2013 Teacher Cohort Training, Phoenix, AZ.

October 21, 2012, McLain, Jean, Trends in Bacterial Antibiotic Resistance in Soils Following Long-Term Biosolids Application ASA-CSA-SSSA Annual Meetings, Cincinnati, OH.

October 27, 2012, Rupprecht Candice and Pam Justice, APW STEM Academy Training, Phoenix, AZ.

October 31, 2012, dos Santos, Plácido, La Gestión del Agua en el Estado de Arizona (Water Management in the State of Arizona.) For visiting dignitaries from the Municipality of La Paz, Baja California Sur, Mexico. Water Resources Research Center, Tucson, AZ.

October 31, 2012, dos Santos, Plácido, El Reciclaje y la Recarga de Aguas Residuales Tratadas en Arizona (The Reuse and Recharge of Treated Wastewater in Arizona.) For visiting dignitaries from the Municipality of La Paz, Baja California Sur, Mexico. Water Resources Research Center, Tucson, AZ.

November 1, 2012, Rupprecht, Candice, APW Water Scene Investigation and C2E, 6th Annual North Texas Regional Water Conservation Symposium, Irving, TX.

November 3, 2012, Schwartz, Kerry, (with Arizona-Sonora Desert Museum), NASA Earth Camp Educator Workshop, Tucson, AZ.

November 3-11, 2012, Megdal, Sharon B., organizer and leader, Israel Water Management Program, tour, meetings and lectures, Israel. (Related media interview aired February 2, 2013 in Israel on IBA the Israeli English news station.)

November 12-15, 2012, Megdal, Sharon B., (Ayoub Ghrair and Othman Almashaqbeh, co-authors), Grey Water Reuse for Agricultural Purposes at Gore-Deir Alla in the Jordan Valley, Deserts and Desertification Conference, Ben Gurion University, Sede Boqer, Israel.

November 12-15, 2012, Megdal, Sharon B., Water Management in Arizona and the Lower Colorado River Basin (USA): Good Practices and Long-term Challenges (Session Organizer, Chair and Presenter), Deserts and Desertification Conference, Ben Gurion University, Sede Boqer, Israel.

November 12-15, 2012, Megdal, Sharon B., (Alice Aureli and Robert Varady, co-authors), Developing a Framework for Groundwater Governance; Deserts and Desertification Conference, Ben Gurion University, Sede Boqer, Israel.

November 12-15, 2012, Megdal, Sharon B., Fostering International Collaboration through the IALC (International Arid Lands Consortium) Seed Grant Program, Drylands, Deserts and Desertification Conference, Ben Gurion University, Sede Boqer, Israel.

November 13, 2012, Megdal, Sharon B., Interview by Patricia Golan, Drylands, Deserts and Desertification Conference, Ben Gurion University, Sede Boqer, Israel.

November 16, 2012, Choate Xiu, Brittany, EnWaP, Northern Arizona Municipal Water Users Association Technical Advisory Committee, Prescott, AZ.

November 26, 2012, Eden, Susanna, Arizona Water Resources, Tucson Garden Club, Tucson, AZ.

November 29, 2012, Megdal, Sharon B., Searching for Water Solutions: Experiences from My Sabbatical and Other Travels, Water Resources Research Center Brown Bag Seminar, Tucson, AZ.

December 1, 2012, Justice, Pam, Earn Your Water Wings, First of a series with twelve sessions for Gilbert and Scottsdale teachers.

December 3, 2012, McLain, Jean, Soil microbial activity within resource islands on semi-arid hillslopes, American Geophysical Union (AGU) Meeting, San Francisco, CA.

December 6, 2012, Schwartz, Kerry, Creating Connection to Foster Action: a Hook for Effective STEM Integration, National Science Teachers Association Regional Conference, Phoenix, AZ.

December 7, 2012, Schwartz, Kerry, and Thomas-Hilburn H., Developing Critical Thinkers through the WIP: Connecting Classroom Practice to Real-world Application, National Science Teachers Association Regional Conference, Phoenix, AZ.

December 7, 2012, Megdal, Sharon B., Israel Water Management Program, Water Resources Research Center External Advisory Committee Meeting, Nina Mason Pulliam Audubon Center, Phoenix, AZ.

December 8, 2012, Schwartz, Kerry, and Colodner, D., The Power of Perspective in Scientific Inquiry: Laurel Clark Earth Camp for Educators, National Science Teachers Association Regional Conference, Phoenix, AZ.

December 8, 2012, Schwartz, Kerry, and Stoll, M.A., Creating Connections to Foster Action: A Hook for Effective STEM Integration, National Science Teachers Association Regional Conference, Phoenix, AZ.

December 10, 2012, Megdal, Sharon B., How Recharge and Water Banking Help Arizona Achieve its Water Management Goals, Visitors from Chile, Tucson, AZ.

December 28, 2012, Megdal, Sharon B., Interview by Sheila Wilensky, “‘Immersed in water’: Sharon Megdal dives into policy and environmental issues,” Arizona Jewish Post, pp. 12, 17, also available on line.

January 9, 2013, Rupprecht, Candice, The Tucson C2E Program, Pima County Local Drought Impact Group, Tucson, AZ.

January 10, 2013, Megdal, Sharon, B., Providing Context for Transboundary Water Management for the Colorado River and Santa Cruz River Systems, Workshop on Transboundary Water Resources Governance and Riparian Areas: Theories, Methods and Applications, University of Arizona, Tucson, AZ.

January 16, 2013, Megdal, Sharon B., Formulating and Conducting Research Projects Relevant to Real-World Problem Solving, Arizona Water Association Research Program, Phoenix, AZ.

January 16, 2013, Thomas-Hilburn, Holly, Water Investigations Program, 2012-2013 Teacher Cohort Training, Phoenix, AZ.

January 16, 2013, Megdal, Sharon B., Formulating and Conducting Research Projects Relevant to Real-World Problem Solving, Arizona Water Association Research Program, Phoenix, AZ.

January 16, 2013, McLain, Jean, University of Arizona Panel Member, Arizona Water Forum, Phoenix, AZ.

January 26, 2013, Megdal, Sharon B., (with Robert Varady) Israeli Water Management and Policy Comparisons with Arizona and Consideration of Some Outstanding Challenges, Secular Humanist Jewish Circle, Tucson, AZ.

January 30, 2013, McLain, Jean, How to Construct an Effective Presentation: It's Not As Hard As You Think!, Guest Lecture, SWES696a (Topics in Soil, Water and Environmental Science)

January 30-February 1, 2013, Mott Lacroix, Kelly and Brittany Choate Xiu, Presentation and visioning session, 6th Annual Little Colorado River Winter Watershed Conference, Show Low, AZ.

February 13, 2013, Megdal Sharon B., Arizona Water Resources Research Center's Information Transfer and Outreach Programs, Annual Meeting of the National Institutes for Water Resources, Washington, DC.

February 14, 2013, Megdal, Sharon B. Providing Context for Transboundary Water Management for the Colorado River and Santa Cruz River Systems, Guest Lecture, RNR 440/540, University of Arizona, Tucson, AZ.

February 20, 2013, Megdal, Sharon B., Transboundary Wastewater Issues in the U.S. and Middle East, Guest Lecture, CPH (College of Public Health) 696R, University of Arizona, Tucson, AZ.

February 26, 2013, Megdal, Sharon B., Interview, Arizona Illustrated, Jane Pointer, Host, KUAT TV, PBS Channel 6, Aired February 26, 2013, Tucson, AZ.

February 28, 2013, Megdal, Sharon B., Interview, Tucson Weekly, Article published February 28, 2013, Tucson, AZ.

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	4	0	0	0	4
Masters	3	0	0	0	3
Ph.D.	5	1	0	0	6
Post-Doc.	0	0	0	0	0
Total	12	1	0	0	13

Notable Awards and Achievements

March 6, 2012. Sharon Megdal was a recipient of a UA at the Leading Edge award announced at UA Innovation Day, She was one of five UA faculty to be recognized for performing cutting-edge research and translating that research into real-world application. Her work on assessing environmental water needs and developing mechanisms for incorporating the demands of all sectors into water planning lead to an innovative mechanism called Conserve to Enhance (C2E). A C2E pilot has been launched in Tucson with the support of many funders and partners.

Kelly Mott LaCroix received the AZ Water's Young Professionals, Fresh Ideas award for her presentation at the 2012 AZ Water conference.

Kelly Mott LaCroix was invited to serve as a delegate at the Center of the American West Student Congress, September 11-14, 2012. The Student Congress was one component of "The Nation Possessed: The Conflicting Claims on America's Public Lands," commemorating the 200th anniversary of the General Land Office, as well as the 150th anniversary of the Homestead Act.

Improving Hydrologic Investigations through Multi-Model Analysis and Discriminatory Data Collection (2010AZ412G) Graduate student, Colin Kikuchi received the following awards: Harshbarger Fellowship (2013) AGU Outstanding Student Poster (2011) University of Arizona Galileo Scholar (2011) Graduate and Professional Student Council Travel Grant (2010)

Does Increasing Solids Retention Time in the Wastewater Treatment Process Affect the Persistence of Antibiotic Resistance Genes? (2012AZ478B) graduate student, Stefan Walston received the following awards: ASM Travel Grant Award (2012) GPSC Travel Award (2012) CALS Fellowship Award (2012) Graduate Representative for the Ag100 Council Meeting (2012) Institute of the Environment Grad Blitz: 1st Place Talk (2012) Institute of the Environment Grad Blitz: Best Science/Society Linkage Talk (2012)

Fate of Emerging Nanoparticle Contaminants during Aquifer Recharge with Treated Wastewater (2012AZ476B) graduate student, Jeff Rottman received the Karecki Award, Engineering Research Center for Environmentally Benign Semiconductor Manufacturing (2013).

Publications from Prior Years